

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN  
RESEARCH ON SMELT-WATER REACTIONS

Interim Report

to

Advisory Technical Committee

1. Interim Activity Report of Project Co-ordinator, IPS Project 2419.
2. Progress Report of The Babcock & Wilcox Company to February 5, 1965.
3. Progress Report of Combustion Engineering, Inc. to February 5, 1965.

March 8, 1965

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS

INTERIM ACTIVITY REPORT OF PROJECT CO-ORDINATOR

TO ADVISORY TECHNICAL COMMITTEE

Project 2419

February 25, 1965

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In view of the tentative nature of research results and the early stage of the research here reported, readers are cautioned against drawing premature conclusions and are advised to await definite recommendations which will be offered when the significance of the technical work has been confirmed and conclusions become warranted.

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THE INSTITUTE OF PAPER CHEMISTRY  
Appleton, Wisconsin

RESEARCH ON SMELT-WATER REACTIONS  
INTERIM ACTIVITY REPORT OF PROJECT CO-ORDINATOR  
TO ADVISORY TECHNICAL COMMITTEE

As an Interim Activity Report, this report differs from previous Activity Reports which have been submitted only a few days or a week previous to a meeting of the Advisory Technical Committee. The recent shift in date of the Advisory Technical Committee meeting from March 15 to April 12, 1965 occurred after the initial drafts of the progress reports of the participating boiler manufacturers had been prepared. It therefore seemed best, in order to keep interested parties informed, to circulate these draft progress reports promptly to those actively associated with the smelt-water research program. This interim report will be superseded, in four weeks, by Report Five in the normal reporting sequence. Report Five will cover activities for the four-month period of November through February, and will be issued to precede the April 12 meeting of the Advisory Technical Committee. We expect that the material of Report Five will later be included in a report to the sponsors of this project.

This interim report covers activities of the Project Co-ordinator from November 15, 1964 to February 25, 1965. Work by the research organizations of The Babcock & Wilcox Company and of Combustion Engineering, Inc. is presented in attached reports, covering the period from November 6 through February 5. The Project Co-ordinator visited the CE Kreisinger Development Laboratory on January 7, the B&W Research Center on January 14, and met with the B&W research group in Cleveland, Ohio, on February 5.

Work on the chemical aspects of smelt-water explosions by Babcock & Wilcox has developed further fundamental information regarding the possibility

of generating explosive gases within recovery furnaces. The production of combustible gases by several mechanisms from smelt-water-char-black liquor systems has been amply demonstrated in this program and in previous work. The problem now is to determine whether or not the gases are generated in sufficient quantity, and in the presence of an ignition source and sufficient oxygen, so that a gaseous explosion results. The B&W program will also explore the possibility of explosions resulting from water and the presence of elemental sodium in the smelt or char bed.

Study of the physical aspects of smelt-water explosions is making encouraging progress at Combustion Engineering. The use of high-speed motion pictures and the measurement of pressure waves is helping to characterize these explosions in more definite terms. Refinements are being made in the technique of producing small-scale laboratory explosions. The effort to develop an additive which would render smelt nonexplosive by preventing the encapsulation of water has sufficient promise to justify the current major emphasis in this direction.

The Project Co-ordinator has continued to explore possible sources of specialized experiences which might contribute to this research project. On December 3, a meeting in Appleton was held with Dr. A. I. Andrews, of the School of Ceramics, University of Illinois, an expert in the field of ceramic enamels. Dr. Andrews felt that we were approaching our smelt additive research problem on a reasonable basis, that we would have to solve the problem experimentally, and that there was little in the way of previous ceramic research or experience that might be useful to us.

On December 7, the Project Co-ordinator visited Professor Lawrence H. Van Vlack, Department of Chemical and Metallurgical Engineering, University of Michigan. He is a recognized leader in the new field of solid state science. He

pointed out that most of the fundamental work in solid state science has been done on simple systems. Our research is dealing with such a complex system that an experimental, rather than a theoretical, approach is likely to be most helpful.

A visit was made on January 5 to Dr. Norbert J. Kreidl, School of Ceramics, Rutgers University. Formerly Director of Materials Research for Bausch & Lomb Optical Company, he confirmed that the viscous nature of glass melts probably prevents the firm encapsulation of water under conditions similar to those which cause explosions when water is in contact with kraft smelts.

On January 7, a conference was held at CE's Kreisinger Development Laboratory with Dr. A. R. C. Westwood, Associate Director of the Research Institute for Advanced Studies, Baltimore, Maryland. B&W was represented at this meeting by Dr. F. O. Ekman. The discussion was directed primarily toward the development of an additive to modify the explosive nature of smelt by weakening any encapsulating shell which might be formed by the addition of water. Dr. Westwood made a number of suggestions on experimental techniques, and proposed several ways of altering the crystalline structure and strength of solidified smelt. We believe that Dr. Westwood may prove to be an effective consultant to this phase of our program.

On January 8, the Project Co-ordinator met in Boston with Dr. F. H. Norton, formerly Professor of Ceramics at M.I.T. and now consulting in affiliation with Arthur D. Little, Inc. He felt that we were conducting a sound program, offered a suggestion for a smelt additive, but did not feel that he was in a position to contribute significantly to our project.

Also on January 8, a general discussion of the research program was held with Professor Glenn C. Williams, Department of Chemical Engineering, M.I.T. He has had a long experience in combustion, explosion, and exotic fuel research

and has agreed to serve as a consultant in the areas of combustion and explosion technology. On January 25, Dr. Williams and the Project Co-ordinator visited the Westbrook, Maine mill of S. D. Warren Company, in order to familiarize Dr. Williams with the normal operating conditions of black liquor recovery furnaces.

On January 9, the Project Co-ordinator visited Professor Woldemar A. Weyl, School of Mineral Industries, Pennsylvania State University, who is an expert in the materials science field. Dr. Weyl was particularly interested in the possibility of elemental sodium contributing to smelt-water explosions, and regarded as reasonable the hypothesis of physical explosions caused by the encapsulation of water in a shell of solidified smelt.

The visit to State College, Pennsylvania, afforded an opportunity for the Project Co-ordinator to talk with Dr. Erik Rosén, who has come from Sweden for a year of postdoctoral research on solid state reactions. From our conversation, it appeared that our program on the chemical aspects of smelt-water explosions at B&W is well informed on the full scope of Dr. Rosén's previous research on recovery furnace reactions, and that Dr. Rosén is not aware of any current research in Scandinavia that might bear on our problem.

An effort is being made to establish a consulting relationship with the Explosives Research Center of the U. S. Bureau of Mines at Pittsburgh, Pennsylvania. This group has an extensive background in combustion, ignition, and explosion technology. Since a continuing consulting arrangement is contemplated, a formal contractual arrangement is necessary, and we are presently engaged in negotiating a mutually satisfactory agreement. It is anticipated that the Explosives Research Center will be particularly helpful in the observation of plant conditions following an explosion, in order to better identify the explosion mechanism responsible for the incident.

It has been recognized that structural analysis of the damage pattern from recovery furnace explosions may also be effective in determining the explosion mechanism. This is a highly specialized field, and there are only a few people who are qualified to undertake work of this type. The possibility of consulting services for damage analysis has been discussed with Professor Robert J. Hansen, Civil Engineering Department, M.I.T., who has an outstanding reputation in this field. A proposal for such work has been received from the Structural Mechanics Section of the Solid Mechanics Research Division of the Illinois Institute of Technology Research Institute. Further discussions will be needed before a definite relationship is established.

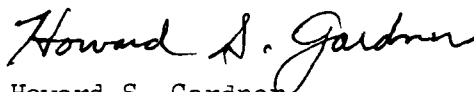
The Project Co-ordinator attended the annual meeting of the Technical Section of the Canadian Pulp and Paper Association, held in Montreal, January 26-29. The meeting provided an opportunity to talk with a number of people in the Canadian industry about experiences relating to recovery furnace safety and to attend a session of papers relating to safe operations of recovery furnaces. Liaison has been maintained with the Subcommittee on Emergency Shutdown Procedures of the Black Liquor Recovery Boiler Advisory Committee.

A visit was made on January 15 and 16 to the mill of Allied Paper Corporation, Jackson, Alabama, to observe conditions resulting from an explosion on January 12. The Project Co-ordinator was accompanied by Wharton Nelson of Combustion Engineering, Inc. and by Joseph M. Kuchta of the Explosives Research Center of the Bureau of Mines. Furnace damage was light, and operations were restored in four days. There were no injuries involved. It appeared that the explosion was caused by combustible gas, with no indication of a smelt-water reaction. It could not be determined whether the explosion was caused by gases from the pyrolysis of black liquor which had been used to quench a corner of the char bed at which a bottom leak of smelt had developed, or whether the explosion

resulted from unburned gas that had accumulated in the furnace during an attempt to light auxiliary gas burners. The full co-operation of the Allied management with our observation of the circumstances of the explosion is greatly appreciated.

In summary, research on the chemical aspects of smelt-water explosions indicates that combustible gases are evolved from some reactions of smelt with water and also from the pyrolysis of black liquor if used to "black out" a char bed during an emergency. To prevent explosions from these sources we already have available or should be able to develop techniques for safe operation, such as inerting or purging furnace atmospheres, use of pilot burners, or elimination of the "blacking out" procedure. The concept of physical explosions caused by the encapsulation of water in a shell of solidified smelt appears to be a useful working hypothesis, not yet proved, but consistent with the known experimental facts. The development of an additive which would prevent physical smelt-water explosions by weakening or preventing encapsulation is a promising approach, although we are working here in a field where there is little fundamental or theoretical information available to guide us. Ultimate success in this research project cannot be predicted with certainty but results to date justify our effort to understand better the mechanisms of smelt-water explosions.

THE INSTITUTE OF PAPER CHEMISTRY



Howard S. Gardner  
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Senior Research Associate  
Administrative Staff



PROGRESS REPORT

FOR THE PERIOD OF NOVEMBER 6, 1964 TO FEBRUARY 5, 1965

TO

H. S. GARDNER, PROJECT COORDINATOR,  
THE INSTITUTE OF PAPER CHEMISTRY

INVESTIGATION OF SMELT-WATER REACTIONS

Submitted by:

THE BABCOCK & WILCOX COMPANY  
RESEARCH CENTER  
ALLIANCE, OHIO

March 1, 1965

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PROGRESS REPORT OF THE BABCOCK & WILCOX COMPANY  
ACTIVITIES ON INVESTIGATION OF SMELT-WATER REACTIONS

INTRODUCTION

This report summarizes the work accomplished between November 6, 1964 and February 5, 1965 and the present status of this project. As outlined in our previous reports, our over-all objective is to determine which chemical reactions occur between the smelt-char-combustion gas system that result in explosive reactions with water. A further objective is to determine the thermal decomposition products of black liquor. Having determined these reactions and reactive products, a basis for preventive measures and procedures can be formulated.

SUMMARY OF WORK

During this report period the following work was accomplished:

1. A large number of possible individual reactions of smelt with water have been examined from a theoretical standpoint. Although most are endothermic, several exothermic reactions could take place and cannot be ruled out at this time as possible causes of explosions.
2. The computer programing, allowing a comprehensive calculation of reaction products, has been completed (assuming condensed phases at unit activity) and the computer time for one problem has been reduced to 5 minutes/run.
3. The equilibrium reaction products for eight different smelt compositions with water at three levels of concentration have been calculated. These results show that small amounts of carbon and sodium sulfate in the sodium sulfide-carbonate smelt result in a large increase in potentially explosive constituents. In general, the lower the ratio of water to smelt, the higher the proportion of

explosive gases.

4. The equilibrium products of the combustion of black liquor solids from 0-120% total air have been calculated. These calculations show that sodium vapor can form at temperatures above 1700°.
5. The volumes of gas resulting from black liquor solids decomposition were obtained as a function of temperature between 600°F and 1800°F.
6. Gas samples taken at each temperature during the black liquor solids decomposition were analyzed. The analysis shows that large amounts of potentially explosive gas are formed.
7. Laboratory tests of the reaction of  $\text{Na}_2\text{S}$  with water vapor showed relatively high yields of hydrogen and hydrogen sulfide.
8. Laboratory studies aimed at determining the equilibrium constant of  $\frac{1}{4} \text{Na}_2\text{S} + \text{H}_2\text{O} = \frac{1}{4} \text{Na}_2\text{SO}_4 + \text{H}_2$  were carried out by the reverse reaction. Results to date show that the reaction equilibrium constant is less favorable toward the production of hydrogen than was expected.

## STATUS

### Chemical Equilibrium Studies

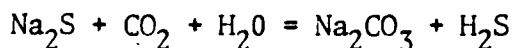
Theoretical studies of the chemical equilibria involved in the Kraft recovery process and smelt-water reactions are being made in order to provide an insight to the chemical reactions which are taking place and to provide guidelines to our experimental work. Two approaches have been used, (1) the consideration of individual reactions of smelt-char-gaseous products with water, and (2) a comprehensive calculation, by computer techniques, of the over-all equilibrium concentrations of individual products expected to exist when the specified reactants are brought together. The first approach is useful as a

very rough guideline to the possible reactions, while the second can be used for more quantitative estimations.

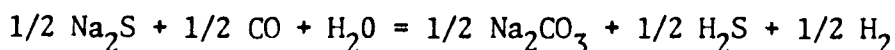
A summary of the individual reactions studied to date is presented in Figures 1-3 in which the log of the equilibrium constant is plotted as a function of temperature. The  $\Delta H$  at 1200°K (1700°F) of the individual reaction is also indicated.

Some caution should be exercised in the interpretation of these reactions as written. First of all, it must be kept in mind that a reaction will proceed, in spite of an unfavorable equilibrium relationship, if one or more products are continuously removed from the reaction, e.g., the formation of gaseous products. Furthermore, if one of the products is initially absent, the reaction will proceed until the concentrations of the products meet the equilibrium criterion. It has been pointed out in previous reports that the thermodynamic properties of  $\text{Na}_2\text{S}$  are not well established; except for  $\text{Na}_2\text{SO}_3$ , the properties of most of the other compounds are reasonably reliable. In the equations presented in Figures 1-3 the data of Rosen<sup>(1)</sup> was used for all reactions.

Equations 1-13 represent the reactions which might be expected from smelt constituents and water. All are written in relation to one mole of water in order to interpret the results on the same basis. Reactions 1-4 were previously discussed in our September 1, 1964 progress report. It was pointed out at that time that the reaction represented by equation (4),



was an exothermic reaction, but that the equilibrium constant became favorable only at lower temperatures ( $\approx 1200^\circ\text{F}$ ). Equation (11) also illustrates an exothermic reaction with a more favorable equilibrium constant which would take place in a reducing atmosphere, such as would exist in the smelt bed.



Equation (9), showing the reaction of water with COS, is also an exothermic reaction with a favorable equilibrium constant. COS would be expected to be a minor constituent of the char bed-smelt atmosphere, as could be inferred from reactions 16-18 shown in Figure 3.

Reactions giving rise to elemental sodium are illustrated in equations 14, 15 and 16. As noted previously, these would be expected to take place at temperatures above 1700°F.

Although the individual reactions listed above are a rough guideline to the mechanism of smelt-water reactions, an over-all calculation of product yields expected from specified reactants is much more meaningful because it takes into account all of the chemical reactions and interactions and furthermore can take into account the laws of mass action. As indicated in previous reports, we have been programing our computer to calculate the equilibrium concentrations of compounds, both gaseous and condensed, which would be expected to be present at equilibrium when specified reactants are brought to equilibrium.

This programing work has now been completed and the method is broad enough to allow a consideration, not only of smelt-water reactions, but also of black liquor combustion and pyrolysis products under a wide variety of conditions. The results of these studies are discussed below and should be viewed in light of the following limitations of the method:

- (1) The method assumes complete equilibrium between reactants and products.
- (2) While the thermodynamic data are reasonably good for most species, the fundamental data for  $\text{Na}_2\text{S}$  has the greatest uncertainty, (our experimental work, described further in the report will serve to reduce such uncertainty to acceptable proportions).

- (3) The method, as it now is used, assumes unit activity for all condensed species. This can cause serious errors in the calculation of the smelt-water reactions but should not affect the combustion calculations to any marked degree. The extent and the direction of this error in the smelt-water reactions can be estimated.

Smelt-Water-Char Reactions - In order to obtain an indication of the relative effects of the components of smelt and char, as well as the effect of variable amounts of water, the following smelt compositions were used as reactants, with water at a ratio of 10#, 1#, and 0.1# of water per 100# of smelt-water mixture.

1. 25%  $\text{Na}_2\text{S}$ , 75%  $\text{Na}_2\text{CO}_3$
2. 35%  $\text{NaS}$ , 65%  $\text{Na}_2\text{CO}_3$
3. 24.75%  $\text{Na}_2\text{S}$ , 74.25%  $\text{Na}_2\text{CO}_3$ , 1% carbon
4. 22.5%  $\text{Na}_2\text{S}$ , 72.5%  $\text{Na}_2\text{CO}_3$ , 5% carbon
5. 24.75%  $\text{Na}_2\text{S}$ , 74.25%  $\text{Na}_2\text{CO}_3$ , 1%  $\text{Na}_2\text{SO}_4$
6. 22.5%  $\text{Na}_2\text{S}$ , 72.5%  $\text{Na}_2\text{CO}_3$ , 5%  $\text{Na}_2\text{SO}_4$
7. 24.66%  $\text{Na}_2\text{S}$ , 73.99%  $\text{Na}_2\text{CO}_3$ , 1.0%  $\text{Na}_2\text{SO}_4$ , 0.338% C
8. 24.41%  $\text{Na}_2\text{S}$ , 73.24%  $\text{Na}_2\text{CO}_3$ , 1.0%  $\text{Na}_2\text{SO}_4$ , 1.338% C

The equilibrium calculations were carried out at 100°K increments between 800°K - 1600°K (981°F - 2421°F).

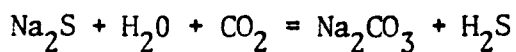
Although all of the results will not be given in this report, illustrative examples of the results obtained for the case (7) and (8) above are shown in Tables I - VI.

As generalities, these calculations have shown the following:

1. The lower the water/smelt ratio, the higher the percent of explosive gas formed. This might explain situations where large amounts of water have entered the smelt bed with no explosion taking place, and further

would indicate that the most dangerous condition would arise if a large surface area of smelt were exposed to a water spray. Thus the physical character of a leak in a boiler pressure part could be significant.

2. The effect of higher sulfidity was largely one of giving increased amounts of  $H_2S$ .
3. Carbon additions to smelt and particularly carbon in the presence of sodium sulfate, gave the highest amounts of potentially explosive gas as well as the highest total volume of gas. This can be interpreted partially as an effect of the water-gas reaction. In the presence of a molten smelt it would not be expected that the water-gas reaction would be self-quenching because of the latent heat content of the smelt. Furthermore, it is significant that relatively small amounts of carbon can contribute substantially to the formation of  $H_2$ ,  $H_2S$ , and  $CO$ .
4. The calculations confirm that at lower temperatures the reaction discussed previously,



takes place with the generation of  $H_2S$ .

5. Sodium hydroxide gas is formed in almost every case at temperatures of  $1700^\circ F$  and above. The significance of this gas is not now apparent except as it contributes to the over-all gas volume generated.

Black Liquor Combustion - In order to determine the conditions which would be expected to exist in the different zones of the furnace, it is planned to carry out equilibrium calculations of products expected under the conditions of variable fuel, a wide range of total air and a range of temperatures. Such calculations will show conditions which may exist in the smelt bed, for example, and give clues concerning the existence of explosion precursors. Initial calculations have been

carried out and have been completed for the case of the combustion of black liquor solids over a range of 0 - 120% total air and 900°k - 1700°K (1161°F - 2601°F).

The basis for the calculations are as follows:

1. Elemental Liquor Analysis:

Na	18.3%
C	42.6
H	3.6
S	3.6
O	31.7
Inert Oxides	0.2

2. Salt Cake Make-up = 4.17 lb/100 lb solids

3. Theoretical air gives smelt of following composition:

Na <sub>2</sub> S	28.5%
Na <sub>2</sub> SO <sub>4</sub>	1.5
Na <sub>2</sub> CO <sub>3</sub>	70.0
	<hr/>
	100.0

This basis is the same as outlined by Clement, Coulter, and Suda<sup>(2)</sup>.

Illustrative results are shown in Tables 7 - 10 for 0, 30, 60 and 100% air. While a thorough discussion of these results will not be attempted in this report, several pertinent items should be noted. The results found at 0.0% air can be considered as a calculation of the theoretical products of decomposition of black liquor solids and show the large amounts of combustible and explosive gas that can be formed. The results at low total air also show that sodium vapor is formed at temperatures above 1701°F. If elemental sodium is soluble in the smelt, small amounts could be present, but whether it exists in significant amounts is a question which will have to be resolved by experiment.

The exothermic reaction of COS with water, discussed previously, raised the question whether significant amounts of COS would be present. These calculations



show that under these conditions, in general, only traces of this gas would be expected. When calculations have been completed of the black liquor solids less the volatile gas, a condition postulated to exist in the bed, more firm conclusions can be drawn concerning the significance of this gas.

It may be noted again in passing that sodium hydroxide is the predominant form of volatile sodium compounds, even at 30% total air.

## EXPERIMENTAL

### Black Liquor Decomposition Studies

In previous reports it has been pointed out gaseous explosions resulting from the release of volatile and explosive decomposition products of black liquor during an emergency shut-down are a distinct possibility. As a result we have previously reported studies showing that black liquor decomposition is essentially an endothermic process and that the black liquor can be considered to decompose in a two-step process. The first step involves the evaporative loss of water and the second step involves the thermal decomposition of the organic solids. In order to further identify the importance of this latter step, experimental work was carried out in order to determine the amount and the composition of the gaseous products.

The moisture was removed from a strong black liquor, with salt cake addition, and known amounts of the black liquor solids were placed in the cool end of a tube furnace arrangement shown in Figure 4. The tube and the sample bottle were evacuated, the furnace brought to the desired temperature and the sample then pushed into the heated zone. The gas pressure produced was measured and the volume corrected to standard conditions. Initial runs at low temperatures (600-800°) showed that a 10 minute residence time in the furnace resulted in release of at least 99% of the volatile material, and this time interval was used as standard. A plot of volume vs time at constant temperatures, is shown in Fig. 5.

The volume of gas, reduced to standard temperature and pressure, resulting from these decomposition studies is shown as a function of temperature in Fig. 6. The plot shows that relatively large volumes of gas result from modest (1200-1400°) temperatures.

Each sample of gas was analyzed for its individual constituents by gas chromatographic methods and the analysis of the gas at each temperature is shown in Table XI.

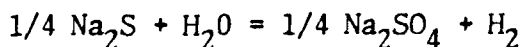
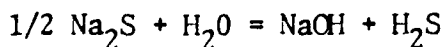
These results show the character of the gases evolved during thermal decomposition. It will be noted that the gas analysis is much different than calculated in Table VII because of the non-equilibrium conditions of the laboratory experiment. At the lower temperatures  $\text{CO}_2$  and  $\text{SO}_2$  are present in relatively large amounts. The percent of  $\text{H}_2\text{S}$  is greatest at lower temperatures, as might be expected. CO is present in large quantities and the  $\text{H}_2$  content becomes significant above 1000°F. We have made rough estimations of the explosive limits of the gases. At 800°F the gas is explosive in air from 21% to 60%. At 1600° the limits are broader and in air it is estimated the gas would be explosive between 7.8% and 59%. It can readily be appreciated that during an emergency shut-down in which black liquor is used for black out that there are significant quantities of explosive gases and water vapor evolved. We are presently working on a more detailed consideration of the implications of the presence of such explosive gases during shut-down.

#### $\text{Na}_2\text{S} - \text{H}_2\text{O}$ Reaction

It has been pointed out in previous reports and in this report that the fundamental thermodynamic properties of  $\text{Na}_2\text{S}$  are not known to a high degree of certainty. As it appears that  $\text{Na}_2\text{S}$  is probably the most reactive chemical in smelt, it is of importance to determine by experiment what the reaction products with water are. Furthermore, if some of the fundamental thermodynamic properties of  $\text{Na}_2\text{S}$  could be determined at the same time, more confidence could be placed on

our equilibrium calculations.

As an initial preliminary test the following experiment was carried out. Helium gas was equilibrated with water vapor and passed over anhydrous  $\text{Na}_2\text{S}$  at  $1650^\circ\text{F}$  at the rate of 0.5 liter/minute. The exit gas was analyzed for  $\text{H}_2$  and  $\text{H}_2\text{S}$  at intervals until the concentration of each was constant. The test apparatus is illustrated in Figure 7, and the results of this experiment are shown graphically in Figure 8. Initially, exceptionally high hydrogen values (in relation to the water vapor present) were found and this amount gradually decreased to a constant value while the experiment was being carried out.  $\text{H}_2\text{S}$  was also found in unexpectedly high concentrations. Apparently two reactions took place,



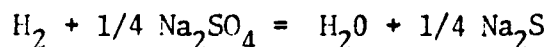
Our interpretation of these results is that the initial high concentrations of  $\text{H}_2\text{S}$  and  $\text{H}_2$  were due to the initial absence of  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_4$  and as a result the reaction was driven to the right. As more  $\text{NaOH}$  and  $\text{Na}_2\text{SO}_4$  formed, equilibrium was ultimately achieved. However, the yield of each gaseous product ( $\text{H}_2$  and  $\text{H}_2\text{S}$ ) was greater than would have been predicted from a consideration of equilibrium constants alone (equations 3 and 5, Fig. 1). Thus it appears that these results indicate that solution effects took place to an unknown degree and illustrate the importance of these effects.

From a practical point of view, this experiment illustrated what could take place in a smelt initially containing neither sodium sulfate nor sodium hydroxide, and demonstrated that significant quantities of hydrogen and hydrogen sulfide can be generated at  $1650^\circ\text{F}$  from the reaction of water with sodium sulfide.

From a theoretical point of view, no fundamental data were obtained because of the complicating factor of solution formation between  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{S}$ , and  $\text{NaOH}$ .

### Na<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub> Reaction

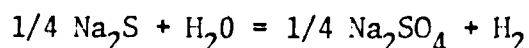
An alternate method of obtaining fundamental thermodynamic data ( $\Delta S$ ) for Na<sub>2</sub>S is to carry out the reaction:



If the hydrogen concentration is kept at approximately 1%, the amount of water estimated to be formed should be insufficient to result in the formation of sodium hydroxide. Thus, solution effects can be eliminated, and the side reaction forming H<sub>2</sub>S should be minimized. In order to eliminate solution effects between Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>4</sub> the reaction must be carried out at temperatures below 1500°F. Although these temperatures are somewhat lower than are of immediate interest, all of the data available indicate that the reaction equilibrium is not affected markedly by temperature. Thus if the equilibrium constant can be determined at the lower temperatures, a relatively safe extrapolation can be made to the higher temperatures of interest.

This experiment was carried out in the following manner. Argon containing 1.08% H<sub>2</sub> was passed over pure Na<sub>2</sub>SO<sub>4</sub> in a tube furnace at flows from 500 cc/min down to 59 cc/min and the exit gas was monitored for hydrogen by gas chromatography. The water formed from the reaction was also measured. Hydrogen concentrations at the two lowest flow levels were constant and equilibrium was considered to be achieved at the lowest flow level. The tests were carried out at 1200°, 1300°, and 1400°F.

Our results have shown that the equilibrium constant for the reaction



is similar to that calculated by Rosen, and Bauer and Dorland<sup>(4)</sup>, but is considerably less than indicated from Mays<sup>(3)</sup> thermal data. The results are compared below:

T (°F)	Equilibrium Constant			
	<u>Experimental</u>	<u>Calculated From Thermal Data</u>		
		May	Rosen	Bauer and Dorland
981°F	---	.093	.038	.041
1200	.041			
1300	.035			
1341		.078	.039	.038
1400	.034			

As these results were obtained at the end of the report period, they should be considered as tentative. To date the full implications of the results have not been evaluated.

#### FUTURE WORK PLANNED

Discussions with the project coordinator have resulted in the following program:

1. A consideration of the implications of the release of explosive gas from (a) black liquor decomposition, (b) smelt-water reactions, and (c) the water-gas reaction.
2. Computer calculations of black liquor combustion simulating the conditions that would be expected to exist in the various portions of the bed and the furnace.
3. Experimental determination of whether elemental sodium plays a part in the explosion mechanism.
4. Experimental determination of the gases released and their explosive potential as a result of a reaction between molten smelt and liquid water.

During the next quarter items (1) and (2) will be completed, and work will be initiated on item (3). In order to carry out item (4), a bench scale containment vessel will be fabricated with its associated pressure measurement and

heating accessories. It is planned to have such a vessel constructed by the middle of the next program quarter and initial tests started by the end of the next report period.

EXPENDITURES

Expenditures to January 31, 1965 are as follows:

Labor plus overhead	\$69,324
Material	<u>10,790</u>
Total	\$80,114

A cost control chart showing actual and anticipated expenditures is attached.

CHA:vlr

Submitted by: C. H. Anderson  
C. H. Anderson

Approved by: W. A. Keilbaugh  
W. A. Keilbaugh, Chief  
Chemistry Section

#### REFERENCES

- (1) Rosen, Erik Trans. Roy. Inst. Tech., Stockholm, No. 159 (1960).
- (2) Clement, J. L., Coulter, J. H., and Suda, S., TAPPI, 46, No. 2, 153A (1963).
- (3) May, M. N. TAPPI, 35, 511-217 (1952).
- (4) Bauer, Thomas W. and Dorland, Rodger M., Can. J. Tech. 32, 91-101 (1954).

TEMPERATURE	800 K ( 981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES( GASEOUS )	VOLUME PERCENT								
CU	.001	.016	.079	.187	.349	.735	1.698	3.628	6.213
CO2	.085	.563	1.666	2.617	3.324	4.907	6.388	14.283	20.242
H2	5.871	5.984	6.143	6.357	6.772	7.002	6.418	4.488	2.062
H2O	90.457	90.360	90.223	89.825	87.921	81.808	68.301	45.357	20.017
H2S	3.586	3.075	1.872	.845	.433	.311	.275	.170	.065
SU2	.000	.000	.000	.002	.007	.022	.078	.233	.566
SO	.000	.000	.000	.000	.000	.000	.001	.005	.017
NA	.000	.000	.000	.000	.002	.018	.113	.524	2.030
NAOH(G)	.000	.001	.016	.167	1.191	5.195	14.725	31.305	48.779
SPECIES( CONDENSED )	LBS / 100 LBS OF FEED								
NA2CO3(C)	69.2362	68.9442	68.2418	67.5878	67.0287	65.6671	62.0801	53.2368	35.8340
NA2S(C)	21.0952	21.2930	21.7749	22.1794	22.2837	22.2218	22.0554	21.7491	20.9174
NA2SO4(C)	.0843	.1154	.1738	.2527	.3882	.5765	.8247	1.2278	2.1274
TOTAL	90.4157	90.3525	90.1904	90.0199	89.7007	88.4653	84.9602	76.2137	58.8788

# EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na<sub>2</sub>S - 24.66%

Na<sub>2</sub>CO<sub>3</sub> - 73.99

Na<sub>2</sub>SO<sub>4</sub> - 1.00

Carbon - 0.338

WATER ADDED: 10#/90# SMELT

TABLE I



TEMPERATURE	800 K	900 K	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K	1600 K
( 981 F )	( 1161 F )	( 1341 F )	( 1521 F )	( 1701 F )	( 1881 F )	( 2061 F )	( 2241 F )	( 2421 F )	
SPECIES( GASEOUS )	VOLUME PERCENT								
CO	6.616	27.244	60.174	72.086	72.514	72.673	71.612	66.650	56.133
CO2	44.008	42.207	20.911	11.135	10.685	10.273	10.191	11.492	15.823
H2	1.206	8.575	14.414	14.418	13.845	13.006	11.160	6.916	2.095
H2O	1.691	5.747	3.471	2.243	2.784	3.218	3.421	3.062	1.759
H2S	38.676	14.664	.904	.090	.044	.026	.017	.009	.004
COS	7.403	1.563	.124	.015	.008	.005	.004	.003	.004
NA2	.000	.000	.000	.000	.000	.000	.000	.003	.014
NA	.000	.000	.000	.000	.007	.087	.604	2.793	7.804
NAOH(G)	.000	.000	.001	.013	.113	.712	2.990	9.067	16.356
SPECIES( CONDENSED )	LBS / 100 LBS OF FEED								
C(S)	.1658	.1309	.0397	.0000	.0000	.0000	.0000	.0000	.0000
NA2CO3(C)	74.6310	74.3117	74.0146	73.9858	73.9821	73.9693	73.9175	73.7425	73.3918
NA2S(C)	24.7085	24.9436	25.1624	25.1834	25.1848	25.1853	25.1855	25.1857	25.1858
TOTAL	99.5053	99.3862	99.2167	99.1692	99.1669	99.1546	99.1030	98.9282	98.5775

# EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na<sub>2</sub>S - 24.66%

Na<sub>2</sub>CO<sub>3</sub> - 73.99

Na<sub>2</sub>SO<sub>4</sub> - 1.00

Carbon - 0.338

WATER ADDED: 0.1#/99.9# SMELT

TABLE III

TEMPERATURE	800 K ( 981 F )	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES( GASEOUS )	VOLUME PERCENT								
CO	.104	.902	2.452	3.789	4.815	5.891	7.499	9.598	10.104
CO2	.719	3.837	7.954	9.724	9.910	10.091	11.454	15.305	21.275
H2	31.192	29.154	25.813	23.493	21.999	20.111	16.185	9.155	2.864
H2O	50.889	53.647	58.011	60.791	61.781	60.295	53.260	37.480	17.971
H2S	17.094	12.446	5.746	2.124	.907	.472	.293	.151	.061
SU2	.000	.000	.000	.000	.000	.001	.003	.017	.161
COS	.013	.013	.018	.011	.007	.005	.005	.005	.008
NA	.000	.000	.000	.000	.002	.025	.174	.796	2.463
NAOH(G)	.000	.000	.006	.071	.578	3.110	11.127	27.491	45.081
SPECIES( CONDENSED )	LBS / 100 LBS OF FEED								
NA2CO3(C)	76.0686	73.6226	69.7112	67.3562	66.3587	65.1485	61.7471	52.3491	34.0491
NA2S(C)	15.0022	16.8033	19.6822	21.3998	22.0041	22.2194	22.2971	22.3456	22.2336
TOTAL	91.0708	90.4258	89.3933	88.7560	88.3628	87.3679	84.0442	74.6948	56.2827

# EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na<sub>2</sub>S - 24.41%  
Na<sub>2</sub>CO<sub>3</sub> - 73.24  
Na<sub>2</sub>SO<sub>4</sub> - 1.00  
Carbon - 1.338

WATER ADDED: 10#/90# SMELT

TEMPERATURE	800 K ( 981 F)	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)
SPECIES( GASEOUS )	VOLUME PERCENT								
CO	6.723	27.524	60.598	79.234	84.156	83.473	64.222	62.674	58.379
CO2	45.435	43.080	21.207	5.647	1.364	.367	.182	.966	3.761
H2	1.095	8.071	13.827	14.072	13.990	12.767	1.694	.716	.127
H2O	1.748	5.465	3.353	1.010	.309	.098	.010	.028	.024
H2S	37.107	14.232	.886	.020	.001	.000	.000	.000	.000
CS	7.891	1.628	.128	.004	.000	.000	.000	.000	.000
NA2	.000	.000	.000	.000	.000	.007	.573	.364	.261
NA	.000	.000	.000	.001	.070	2.624	32.068	32.230	33.487
NAH	.000	.000	.000	.000	.000	.004	.021	.015	.007
NAOH(G)	.000	.000	.001	.012	.110	.658	1.230	3.008	3.953

LBS / 100 LBS OF FEED

SPECIES( CONDENSED )									
C(S)	1.1741	1.1379	1.0433	.9748	.9526	.9342	.0000	.0000	.0000
NA2CO3(C)	73.8447	73.5182	73.2152	73.1829	73.1785	73.1086	68.8319	68.4895	67.9438
NA2S(C)	24.4484	24.6889	24.9120	24.9356	24.9363	24.9363	24.9364	24.9363	24.9363
TOTAL	99.4673	99.3450	99.1705	99.0933	99.0675	98.9792	93.7682	93.4258	92.8801

# EQUILIBRIUM COMPOSITION OF SMELT-WATER REACTIONS

SMELT COMPOSITION: Na<sub>2</sub>S - 24.41%

Na<sub>2</sub>CO<sub>3</sub> - 73.24

Na<sub>2</sub>SO<sub>4</sub> - 1.00

Carbon - 1.338

WATER ADDED: 0.1#/99.9# SMELT

# EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

PRESSURE: 1.00 ATMOS.		PER CENT TOTAL AIR:					.0		
TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES( GASEOUS )									
VOLUME PERCENT									
CU	11.564	29.473	38.077	40.333	44.142	46.750	46.918	46.931	46.678
CO2	7.605	5.017	1.304	.313	.103	.038	.015	.007	.003
H2	51.135	55.532	57.394	57.679	46.769	40.227	40.219	40.174	39.726
H2O	14.547	6.550	1.980	.611	.191	.071	.033	.017	.009
CH4	8.408	3.008	1.196	.527	.171	.069	.040	.025	.016
H2S	6.688	.409	.009	.000	.000	.000	.003	.033	.269
COS	.051	.007	.000	.000	.000	.000	.000	.001	.011
NA2	.000	.000	.000	.000	.044	.081	.055	.037	.028
NA	.000	.000	.003	.210	6.825	12.072	12.492	12.669	13.173
NAH(G)	.000	.000	.000	.001	.021	.038	.044	.048	.053
NAOH(G)	.000	.002	.035	.324	1.733	.652	.180	.057	.021
LBS / 100 LBS OF FEED									
SPECIES( CONDENSED )									
C(S)	29.6999	26.2034	24.0616	23.4190	20.4136	17.1166	16.8598	16.7920	16.7678
NA2CO3(C)	42.9492	30.1943	29.0540	28.2586	12.5749	.0000	.0000	.0000	.0000
NA2S (C)	.4436	9.8339	10.6344	10.6546	10.6552	10.6547	10.6458	10.5412	9.6380
TOTAL	73.0926	66.2315	63.7500	62.3321	43.6437	27.7713	27.5056	27.3331	26.4057

# EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

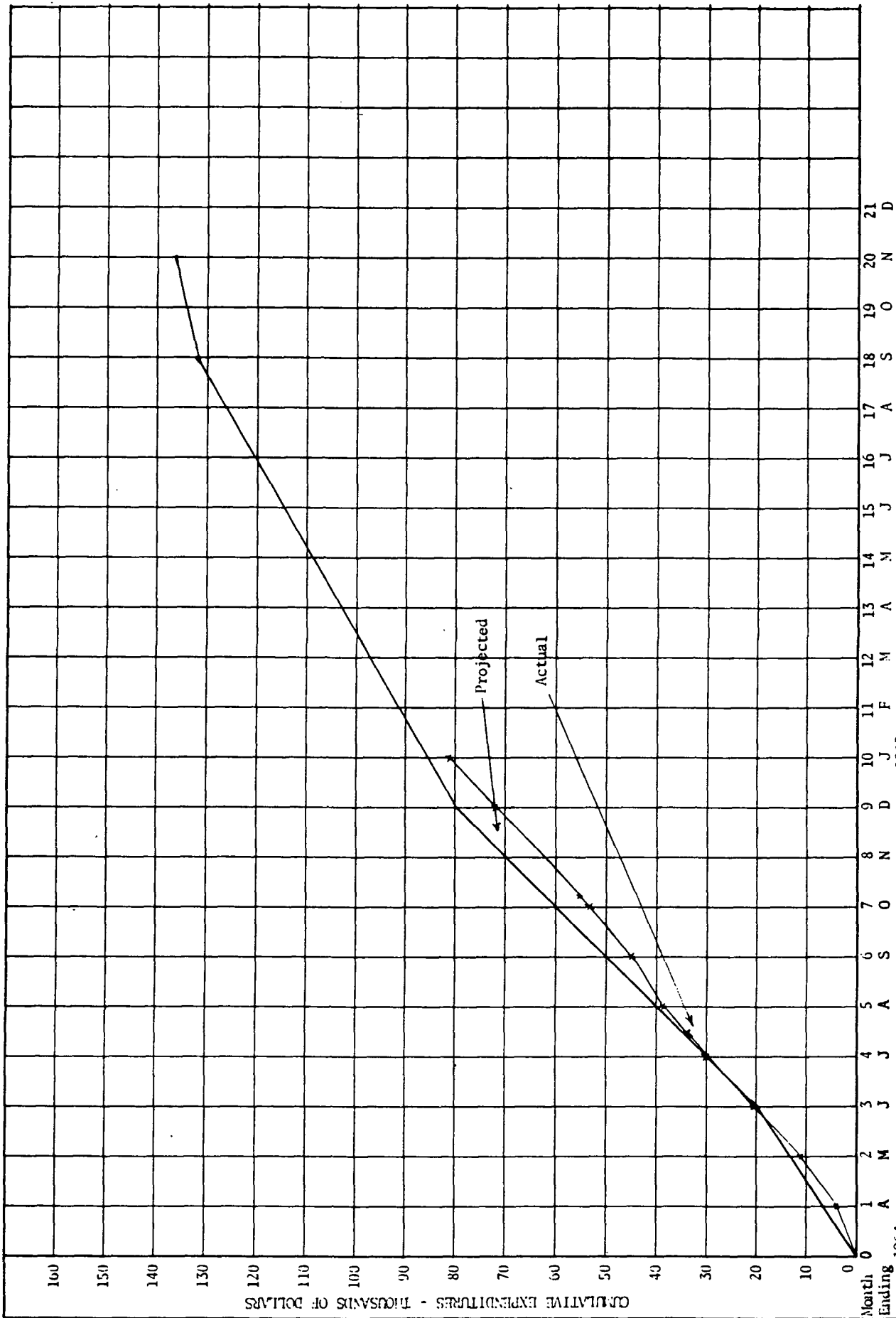
PRESSURE: 1.00 ATMOS.		PER CENT TOTAL AIR: 60.0							
TEMPERATURE	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)
SPECIES( GASEOUS )									
VOLUME PERCENT									
CO	11.123	12.292	12.995	13.676	14.315	14.928	15.290	15.785	16.028
CO2	12.309	11.404	11.144	10.638	10.287	10.439	9.949	9.136	8.841
H2	9.394	8.738	7.936	7.184	6.311	4.941	4.475	4.096	3.978
H2O	4.497	5.617	6.856	7.626	7.939	7.443	7.475	7.063	7.433
CH4	.162	.006	.000	.000	.000	.000	.000	.000	.000
N2	61.440	61.106	60.756	60.549	59.923	58.016	57.779	57.124	56.968
H2S	1.032	.798	.275	.120	.063	.046	.246	.442	.305
SO2	.000	.000	.000	.000	.000	.000	.009	.061	.141
SO	.000	.000	.000	.000	.000	.000	.001	.010	.028
COS	.041	.037	.015	.008	.005	.005	.029	.059	.043
S2	.000	.000	.000	.000	.000	.000	.022	.212	.239
NA	.000	.000	.000	.004	.039	.243	.435	.857	1.151
NAOH(G)	.000	.001	.022	.196	1.118	3.939	4.289	5.154	4.843
LBS / 100 LBS OF FEED									
SPECIES( CONDENSED )									
NA2CO3(C)	11.2151	10.4042	8.4705	7.5931	5.6808	.0000	.0000	.0000	.0000
NA2S (C)	.0000	.5955	1.9922	2.4084	2.5608	2.6017	1.8417	.0000	.0000
TOTAL	11.2151	10.9997	10.4627	10.0015	8.2416	2.6017	1.8417	.0000	.0000

# EQUILIBRIUM COMPOSITION OF COMBUSTION PRODUCTS OF BLACK LIQUOR

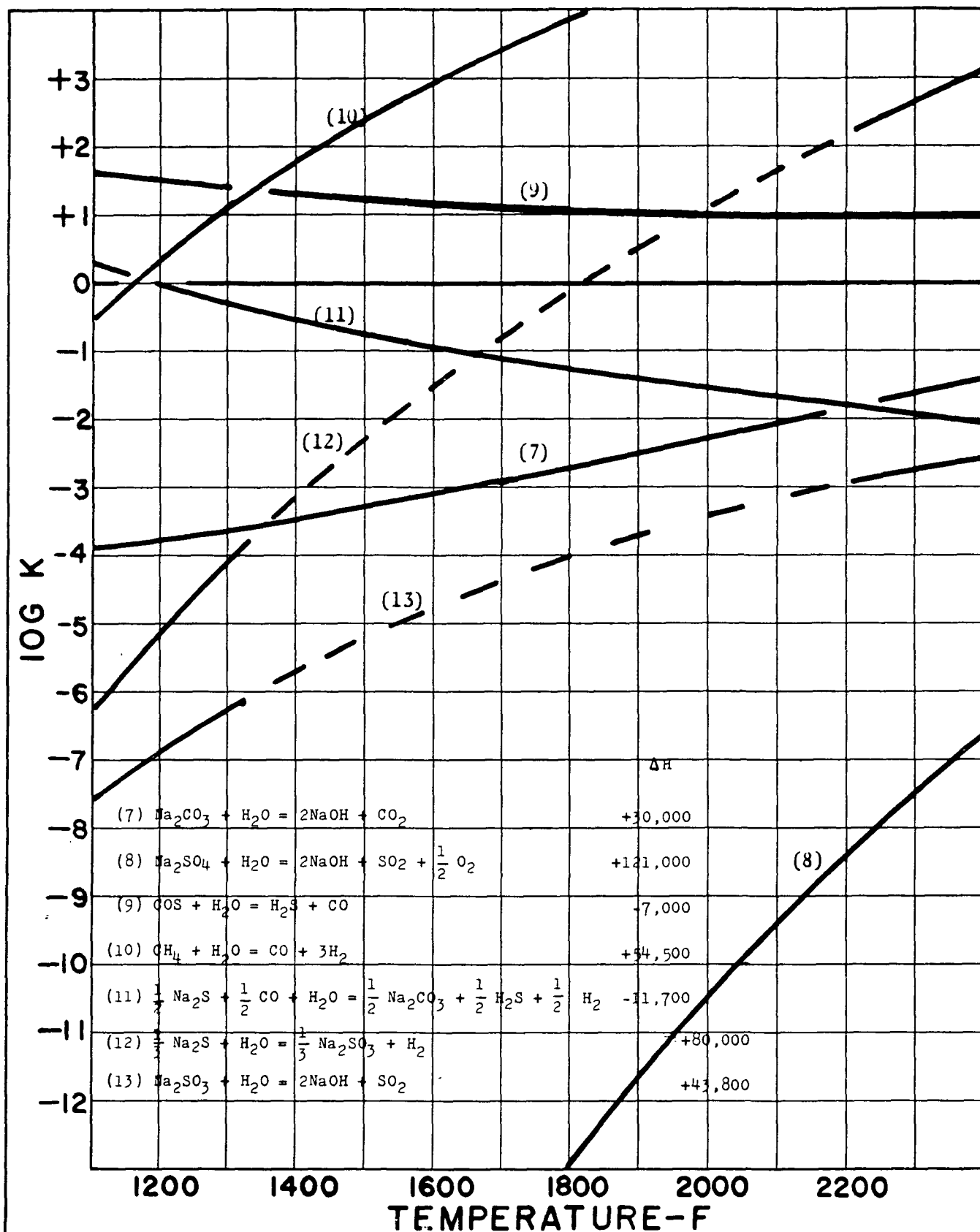
TEMPERATURE	PRESSURE: 1.00 ATMOS.					PER CENT TOTAL AIR:				
	900 K (1161 F)	1000 K (1341 F)	1100 K (1521 F)	1200 K (1701 F)	1300 K (1881 F)	1400 K (2061 F)	1500 K (2241 F)	1600 K (2421 F)	1700 K (2601 F)	
SPECIES( GASEOUS )	VOLUME PERCENT									
CO	.222	.506	.922	1.387	1.744	1.869	1.448	1.473	1.474	
CO2	16.558	16.358	16.056	15.752	15.727	16.262	16.470	16.441	16.433	
H2	.329	.471	.600	.676	.638	.477	.290	.257	.228	
H2O	10.590	10.549	10.533	10.476	10.075	8.944	8.475	8.533	8.590	
N2	71.774	71.695	71.979	71.359	70.693	69.105	68.291	68.271	68.250	
H2S	.513	.398	.256	.120	.037	.011	.004	.001	.000	
SO2	.001	.003	.010	.027	.052	.128	.703	.708	.708	
COS	.012	.014	.013	.008	.003	.001	.001	.000	.000	
NA	.000	.000	.000	.001	.009	.050	.096	.143	.202	
NAOH(G)	.000	.002	.023	.189	1.018	3.150	4.215	4.167	4.106	

SPECIES( CONDENSED )	LBS / 100 LBS OF FEED				
	NA2CO3(C)	NA2SO4(C)	TOTAL		
NA2CO3(C)	6.7541	6.4082	5.9427	3.6101	.0000
NA2SO4(C)	.9993	1.4596	2.0351	2.8993	.0000
TOTAL	7.7534	7.8677	7.9778	6.5094	2.6774

TABLE X



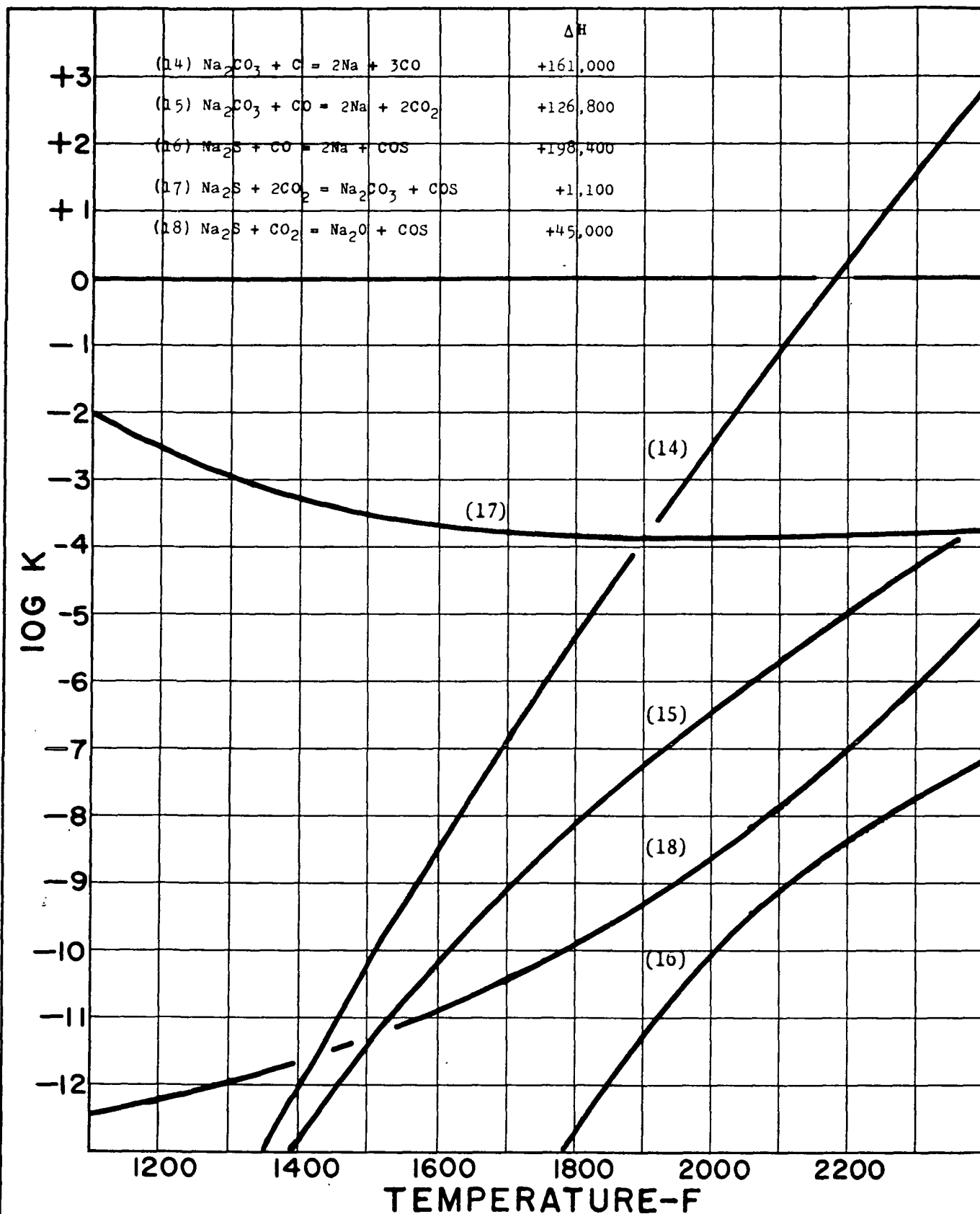
SUBJECT: ANTICIPATED EXPENDITURE VS. TIME CURVE, INVESTIGATION OF SMLT-WATER REACTIONS FOR FOURMILNER KRAFT INSTITUTE		FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO	
BY		DATE	DRAWING NO.	
REV.		REV.		



SUBJECT	EQUILIBRIUM CONSTANT AS		FILE NO.
	A FUNCTION OF TEMPERATURE		BY
			DATE
			REV.

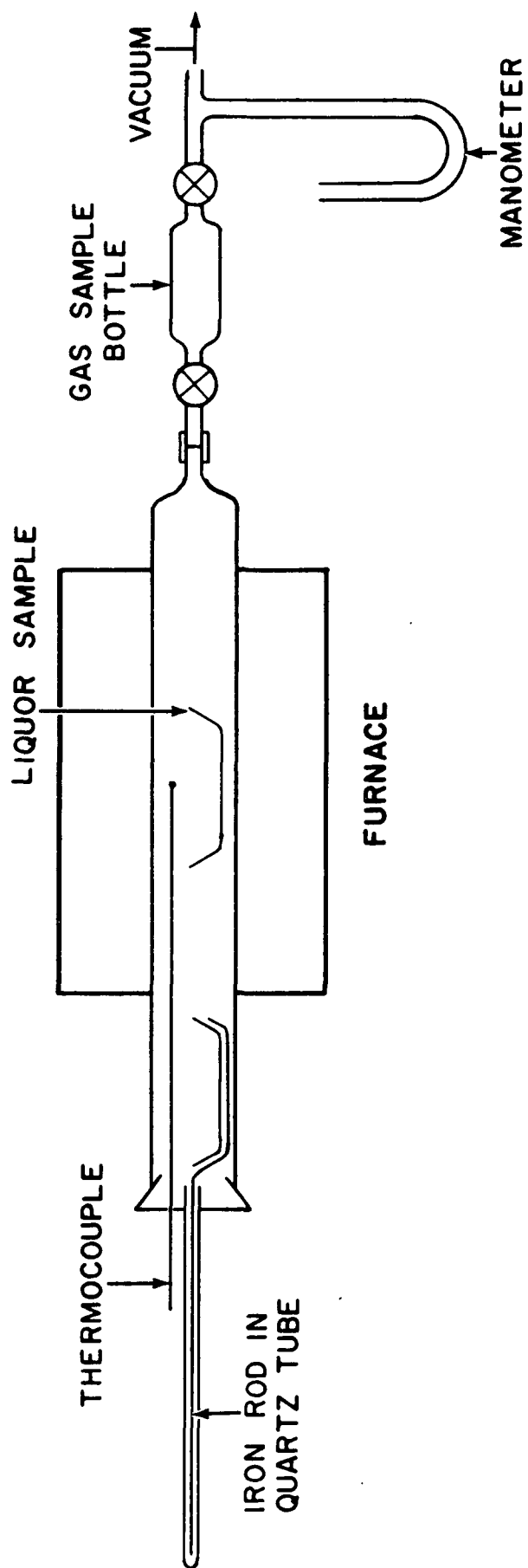
FIGURE 2





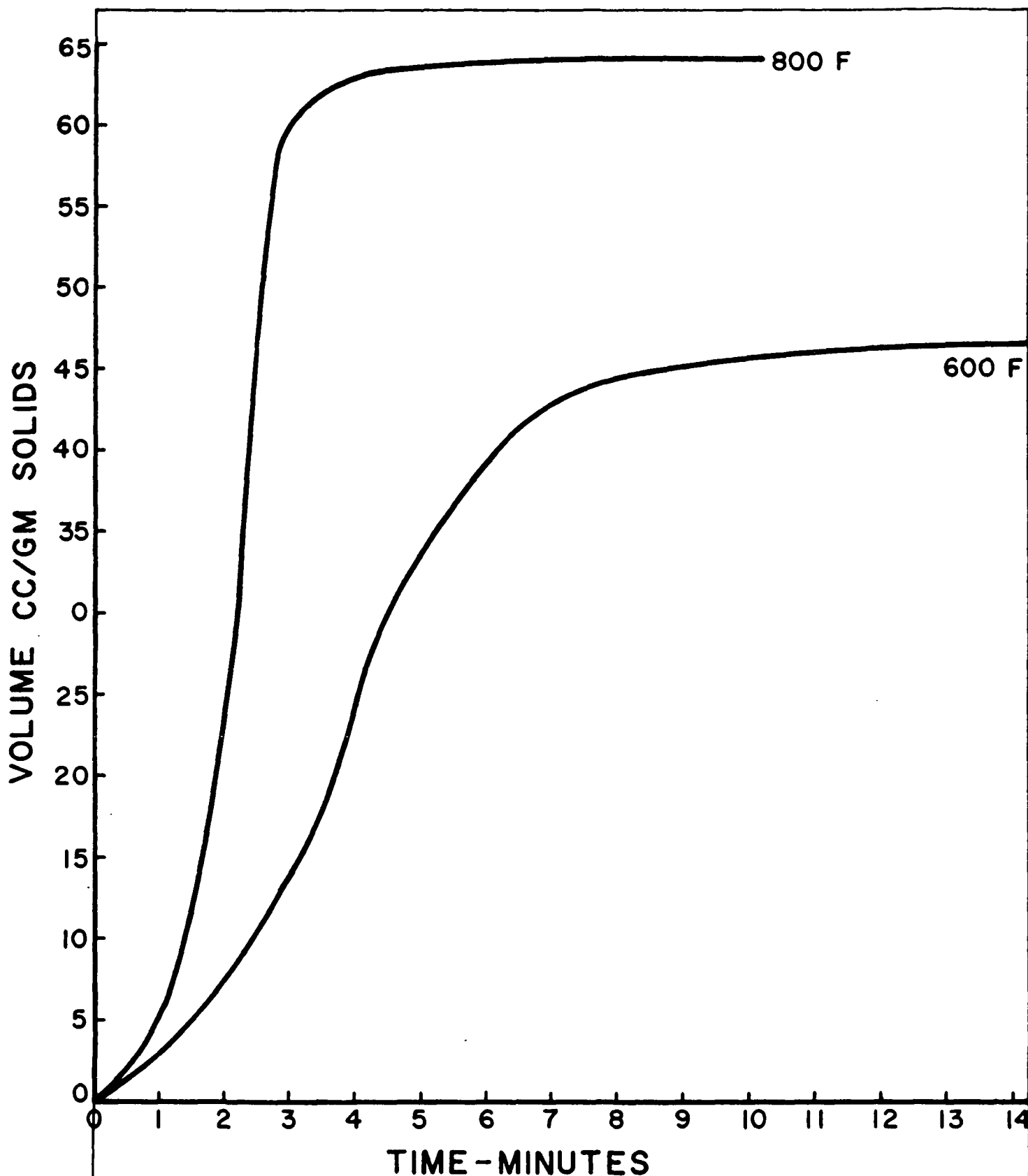
SUBJECT EQUILIBRIUM CONSTANT AS A FUNCTION OF TEMPERATURE	FILE NO.
	BY
	DATE
	REV.

FIGURE 3



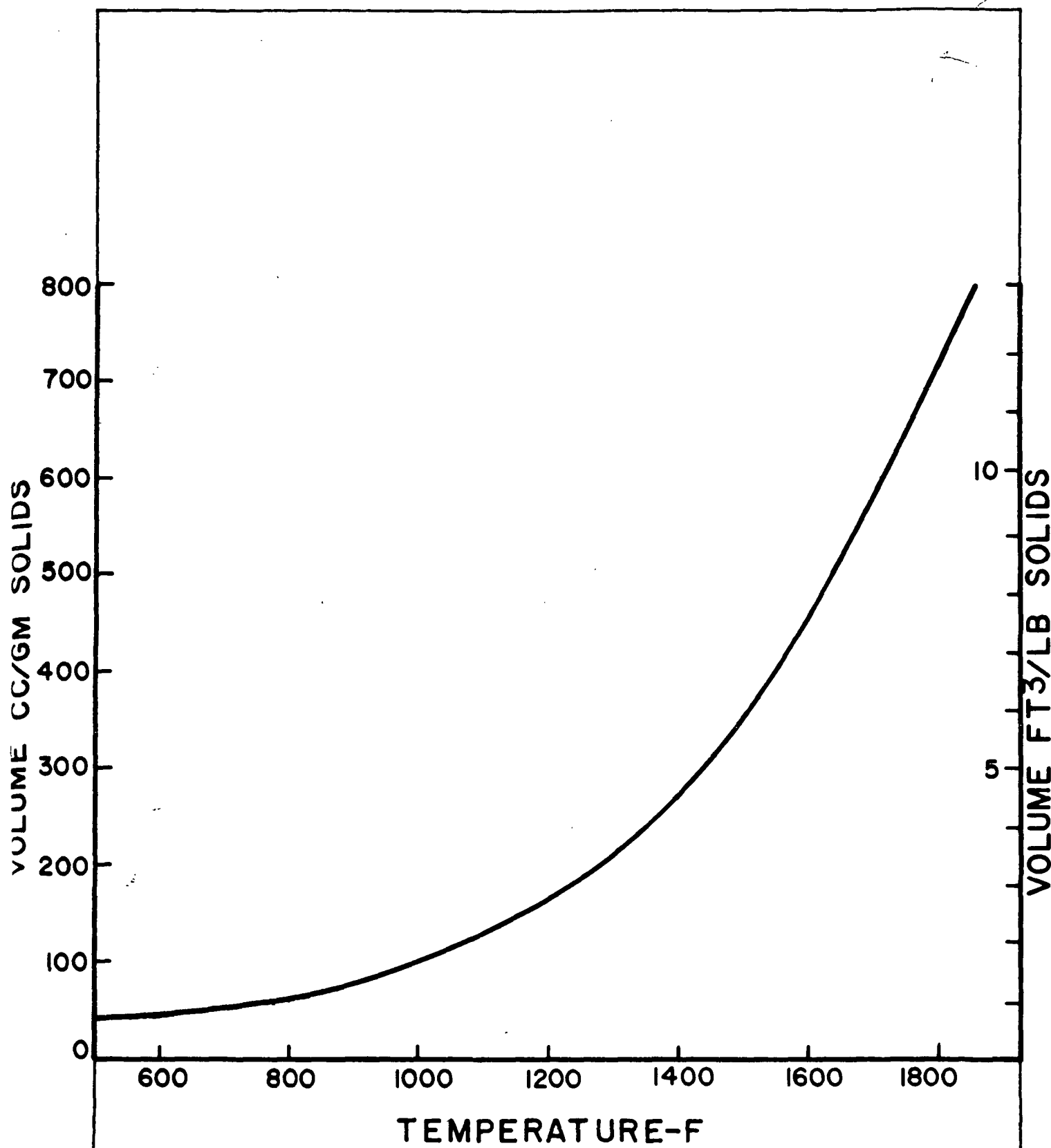
BLACK LIQUOR  
DECOMPOSITION FURNACE

FIGURE 4



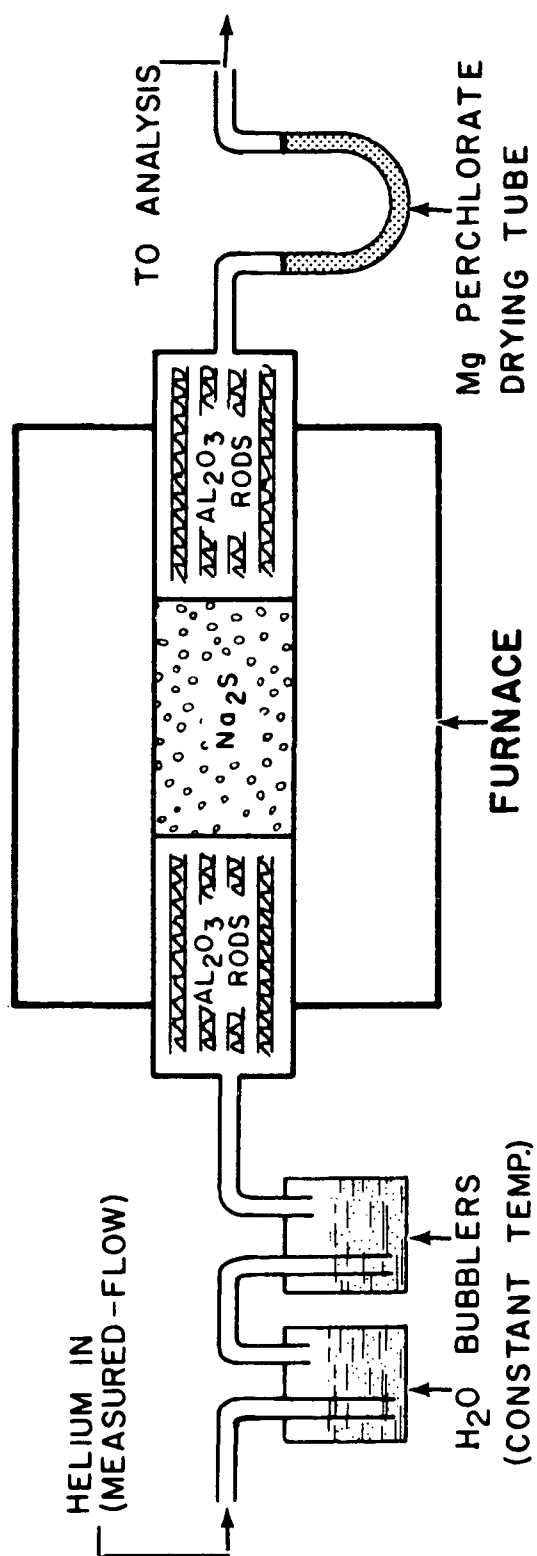
SUBJECT VOLUME OF GAS EVOLVED (STP) FROM BLACK LIQUOR SOLIDS AS FUNCTION OF TIME	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	SCALE	
	DRAWING NO.	

FIGURE 5

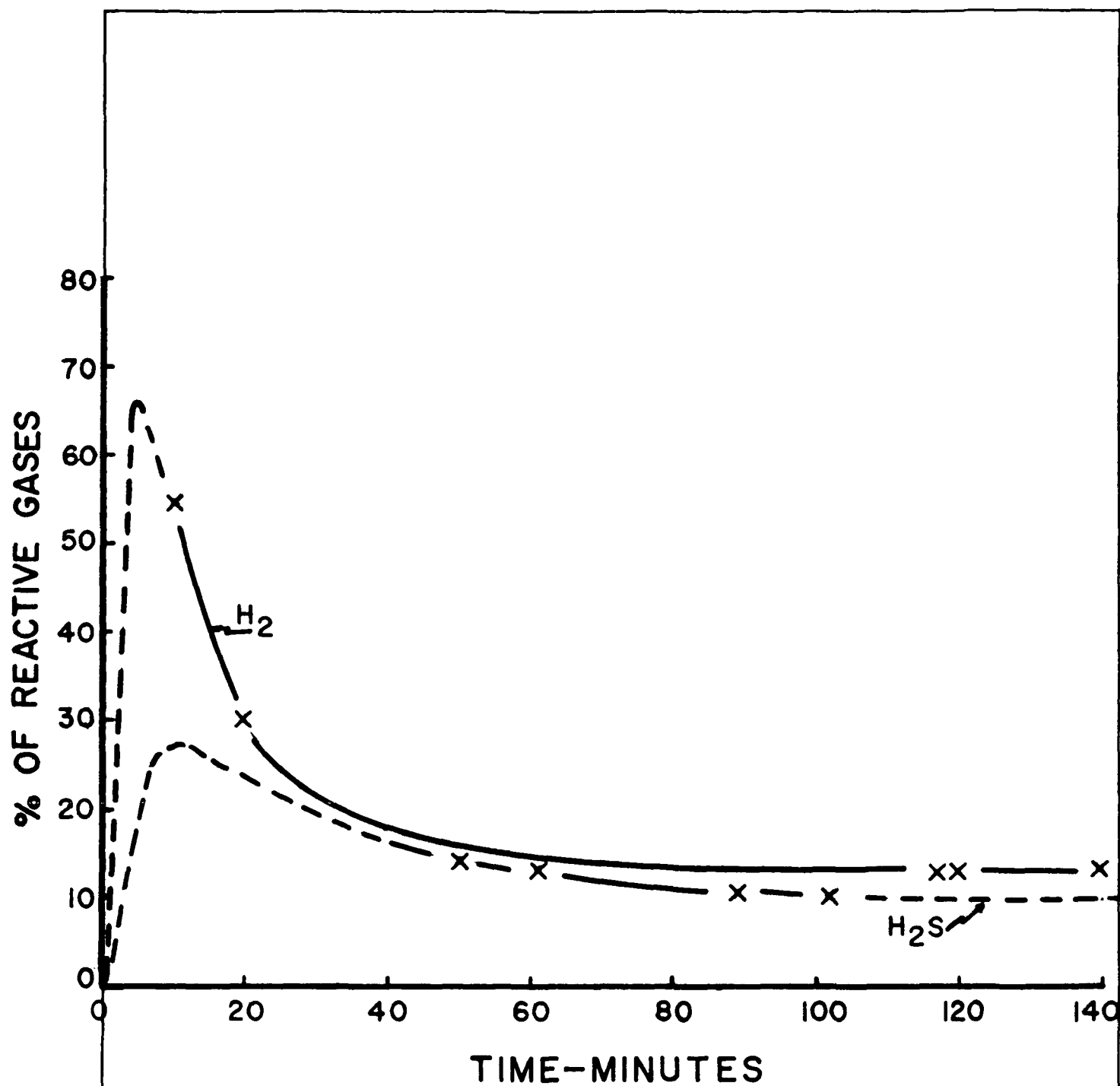


SUBJECT VOLUME OF GAS EVOLVED FROM BLACK LIQUOR SOLIDS AS FUNCTION OF TEMPERATURE	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	SCALE	DRAWING NO.

FIGURE 6



TEST APPARATUS  
FOR  $\text{H}_2\text{O}$  (VAPOR) -  $\text{Na}_2\text{S}$  (SOLID) REACTION STUDIES



YIELD OF  $H_2$  AND  $H_2S$  FROM  
 $H_2O - Na_2S$  REACTION (1650 F)

SUBJECT	FILE NO.	THE BABCOCK & WILCOX CO. RESEARCH CENTER ALLIANCE, OHIO
	BY	
	DATE	
	SCALE	DRAWING NO.

TRIMONTHLY PROGRESS REPORT  
COVERING WORK FROM NOVEMBER 6, 1964 THROUGH  
FEBRUARY 5, 1965

to

Dr. H. S. Gardner, Project Coordinator  
The Institute of Paper Chemistry

Submitted by  
Combustion Engineering, Inc.  
Kreisinger Development Laboratory  
Windsor, Connecticut

This study is being conducted by Combustion Engineering, Inc. for the Board of Directors, Smelt-Water Research Group. No reproduction or other use of the information contained herein is permitted without the written approval of the Advisory Technical Committee, Combustion Engineering, Inc., The Babcock & Wilcox Co., and The Institute of Paper Chemistry.

NO. 4 PROGRESS REPORT ON  
THE COMBUSTION ENGINEERING PROGRAM FOR  
DETERMINING THE NATURE OF AND REMEDIES FOR  
EXPLOSIVE REACTION(S) BETWEEN SMELT AND  
WATER IN KRAFT CHEMICAL RECOVERY FURNACES

Encapsulation Mechanism Theory

(Supporting evidence for some facets of the theory which follows are presented in the later sections on experimental results.)

Liquid water has a uniquely high specific heat (heat capacity) and latent heat of vaporization compared with other fluids. This is due in large part to its hydrogen-bonded structure which greatly restricts molecular movement on heating. The nature of the molten material (metal or ceramic) also is important, and according to this theory, must allow the almost instantaneous generation of a frozen shell having considerable tensile strength when water is placed beneath melt surface at appropriate temperatures for both liquids.

Submerging liquid water beneath melt of proper composition is believed to result in the following concurrent processes:

- (a) A very high initial heat transfer rate occurs between molten melt and encapsulated liquid water which increases frozen shell thickness rapidly.
- (b) The high heat absorbing capacity of water (and low specific heat of most molten materials) causes a relatively thick containing shell of solid to freeze per unit weight of water compared with other fluid coolants.
- (c) A sizeable time delay (on the millisecond scale), compared with immersion of gases or other liquid coolants, occurs during which internal capsule pressure fails to outrace the increasing shell strength (thickness).

The net result of a, b, and c, is that frozen shell thickness forms fastest initially when the pressure inside the capsule is the lowest. Thus encapsulation explosions may be made possible in part by the unique physical properties of water itself. Delay created by racing of these two opposing processes, i.e., the pressure buildup, and increasing shell thicknesses to contain it, allows rapid storage of thermal energy as hot water and steam under pressure in the capsule. Rupture of the capsule liberates this stored energy much more rapidly than it was stored. Mechanical



PV work is done by rapidly expanding steam from the explosion.

An encapsulation explosion in kraft smelt may be analogous in some respects to heating a compressed nitrogen cylinder until a physical explosion occurs. This explosion is due solely to the sudden release of stored thermal energy by rupture of the walls. No chemical change is involved in the process. Here also energy stored at a comparatively leisurely pace during heating can be liberated very rapidly by bursting of the shell. Using this concept, we have postulated a model of the pressure vs. time sequence inside a capsule in kraft smelt to explain what happens, assuming subcritical conditions. These points are illustrated by the theoretical diagram and graphs of Fig. 1:

- (1) A volume of water is placed under the surface of the molten smelt at time A. A strong encapsulation shell of frozen smelt forms almost immediately around this submerged volume of water and some surrounding steam blanket, and increases in thickness rapidly.
- (2) A sizable induction period AC occurs in which water inside the capsule absorbs heat very rapidly from the surrounding body of hot molten smelt. This heat passes through the thickening frozen shell. Pressure inside the capsule increases rapidly during this period because of the efficient heat transfer caused by a large  $\Delta T$  and a relatively thin shell.
- (3) Shell strength (thickness) to contain this pressure increases less rapidly after the initial containment shell forms due to: (a) a decreasing temperature differential between the smelt and water, and (b) the increasing distance required for heat of fusion to travel to the water.
- (4) Shell rupture B (explosion) occurs when pressure build-up wins this race, releasing steam and/or hot water in atomized condition into the main body of surrounding molten smelt. Capsule pressure quickly assumes atmospheric value, following line BD.
- (5) PV energy stored in the capsule is liberated as an explosion wave in the very brief time interval CD. Compare this with much longer interval AC required for energy storage.

Quick energy release is an inherent characteristic also of condensed phase explosives like TNT, which on detonation creates large volumes of gases almost instantaneously by chemical reactions. Here useful mechanical work is accomplished due to: (a) the tremendously rapid (in the millionth of a second range) release of energy and (b) the concentration of energy release in the small volume occupied by the explosive itself, rather than to an inherently large quantity of energy produced from a unit weight of

the explosive. The damage effects of physical and chemical explosions are similar in type since both are caused by rapid release of gases under high pressure. The release rate from encapsulation explosions has been found to be almost a thousand times slower than that from TNT in the small scale tests conducted to date so that the two would probably not be comparable in extent of damage. Both, however, free a large amount of energy per unit volume of original exploding (condensed phase) material. Mechanisms of chemical and physical explosion processes are different in some important respects. For instance the proposed existence of an encapsulation shell in physical explosions provides hope for a successful plant remedy as outlined in a later section of this report.

## Experimental

### (A) High Speed Movies

Mr. Tung Nathan, Mr. Charles Norton, and Mr. Douglas Wayne of this laboratory developed the successful photographic and explosion techniques described in this section.

It was decided to take high speed color movies of water injections into molten kraft smelt in order to gain a better idea of what happens in an explosion and the detailed sequence of events preceding it. Perhaps one could even photograph a capsule before it exploded if light could be made to penetrate far enough below smelt surface. Pictures taken with an ordinary movie camera at 32 frames per second were not nearly fast enough to reveal the necessary details of an explosion process. A model K1004 Hycam motion picture camera (16mm. x 400 ft.) was rented. It can vary taking speed from 10 to 20,000 pictures per second without changing the motor. Tri X black and white film (ASA 200) produced pictures too grainy to be useful. Also it did not give the details provided by color film. Most of the pictures to date have been on High Speed Ektachrome ERB (ASA 125, which is increased to 250 by special development). Use of 400 foot lengths of film allowed placing both injection and explosion on one reel at a speed of 5600 frames per second.

Manual synchronization of the explosion to starting of the camera was employed effectively. Photoflood lights and several types of ordinary stand-mounted photographic flood lights did not give enough illumination. Next, a series of four Sylvania FF33 long duration flash lamps were placed on four corners of a square surrounding frame less than a foot away from the crucible of molten smelt. They were fired by a cam-operated sequence timer after water injection so that each (after the first) would fill in the "tail off" period of its predecessor. This arrangement provided almost enough light to give the needed details, but the shifting direction of illumination as each bulb fired produced confusing shadows. The problem of gaining sufficient illumination has been a difficult one at the high speeds used. The next efforts will be made as suggested by the Bureau of Mines using a

movie type carbon arc projector, or a specially designed high intensity light with condensing lens system to concentrate light on the surface of smelt in the crucible. Prints of some of these pictures will be included in the next progress report. Movies will be shown at the next meeting of the Advisory Technical Committee.

Injectons of room temperature 10% green liquor (10% kraft smelt dissolved in water) were found to increase the certainty of an explosion on first injection, when in addition the smelt was cooled to 1600°F. This is about mid-point of the temperature range in which kraft smelt explodes with successive water injections.

Although improvement in movie quality, particularly lighting, is desirable, the explosion and prior events were correctly framed in speed. The following points were established from careful examinations of three films:

- (1) No flame was evident in any explosion or in events leading to it. Only glowing particles of finely divided smelt were observed during all explosions.
- (2) There was a fairly consistent 0.030 second (30 milliseconds) delay between the completion of green liquor injection and the resulting explosion. The surface of the smelt was turbulent following a water injection.
- (3) The explosion itself was very rapid and required only about 2 milliseconds.
- (4) Explosions were initiated from a source of limited area (approx. 1/2" diameter) below smelt surface, exactly where liquor injection had been made.

All of these observations fit the theoretical model proposed for a physical encapsulation explosion. Incidentally, it has been found that the "firecracker-like" odor produced by explosions is due to smelt dust and is eliminated almost entirely when the observer wears a dust filter mask. The smelt used (30% Na<sub>2</sub>S) was opaque over the entire molten temperature range 1450° to 2000°F., so it was not possible to see through any appreciable depth. Other compositions of materials, like 80% Na<sub>2</sub>CO<sub>3</sub> with 20% NaCl, also explode violently on water injection and are considerably more transparent. It may be possible to photograph an encapsulation produced by injecting water into melts like this one.

#### (B) Pressure Wave Measurements

(Mr. Charles Norton, Research Engineer, shared in the development of techniques and data reported in this and following

sections). Considerable interest lies in accurately measuring the speed and amplitude of shock waves produced by explosions from water injected into molten smelt. Effort has been made to keep explosions down to a scale which will not damage the plywood explosion barrier or operating personnel. This has been accomplished by regulating the volume of water to individual successive injections of 3 cc., about 60 drops. The violence produced is surprisingly great from even this small quantity of water. It increases as the smelt temperature at which explosions take place increases within the 1470-1670°F range mentioned in earlier reports. This range can be altered by changing the smelt composition.

The pressure wave measurements have been continued using the Visicorder with a new high speed drive. Increased chart speed has allowed a more accurate assessment of the duration of pressure waves produced. They have averaged 1 to 3 milliseconds, which is about a thousand times slower than waves from condensed phase chemical explosives. This direct transducer measurement agrees well with the photographically calculated value reported in section (A). It is possible that these speeds may scale up when larger injections are used in the spherical high pressure explosion vessel.

Mr. R. W. Watson of the Bureau of Mines mentioned on our February 3-4 visit that there is strong reason to doubt the efficient transfer of shock wave energy from molten smelt to air. Thus the current technique for estimating explosion pressures at the capsule itself may have to be modified so that a metal rod transmits this wave to a directly-coupled transducer diaphragm. In the present state, however, the transducer setup does permit valid conclusions about the number of explosions, the time between them, their speed, and their relative intensity.

### (C) Effect of Water Temperature and Dissolved Smelt

Several further experiments on the effects of composition of the aqueous phase and its temperature seemed in order. Table 1 which follows shows the results from successive 3 cc. injections of aqueous material in molten 1800°F. synthetic kraft smelt (30% Na<sub>2</sub>S) until an explosion or solidification resulted.

<u>TABLE 1</u>		
<u>Solution Injected</u>	<u>Results</u>	<u>Smelt Temp. (°F) for Explosion</u>
1) Blank - 68°F. Water	Violent explosion	1650
2) Blank - 68°F. Water	Violent* explosion	1585
3) 176°F. Water	Violent* explosion	1503
4) 187°F. Water	None	-
5) 203°F. Water	None	-
6) 203°F. Water	None	-
7) 205°F. 10% Green Liquor	Violent* explosion	1640
8) 212°F. 10% Green Liquor (tube leak)	Three moderate explosions	Unknown

\*Shattered crucible

Runs No. 1 and 2 reconfirmed many previous experiments showing the violent explosions which almost invariably result if cool water is suitably submerged beneath the surface of molten smelt. Runs 3, 4, 5, and 6 established the fact that water hot enough will not explode under the same conditions of mixing with smelt. These results posed the question of how hot water from a ruptured boiler tube can cause explosions. Run No. 7 in which hot green liquor made by dissolving 10% smelt in water was injected into smelt showed that inclusion of dissolved salts can override the explosion-preventing effect of very hot water. Run No. 8 with 212°F. 10% green liquor added in a continuous stream (102 cc/15 seconds) to the surface of the molten smelt (rather than below it) to simulate a small tube leak gave three moderate explosions in quick succession. This confirmed results of the previous experiment which used forcible injection of green liquor below smelt surface.

Results of these tests agree exactly with conclusions of the previous 1956 study (1) on dissolving tank explosions. I.e., hot water (if it is hot enough) lessens smelt-water explosions. Salts dissolved in the water make its explosive reaction more violent with molten smelt. These results also imply that water standing on smelt in a chemical recovery furnace probably increases the chance of an explosion with time (within limits) due to:

- (a) increased dissolved smelt content in the water.
- (b) reduced temperature of the water.
- (c) reduced temperature of the smelt to 1670°F, but above 1470°F.

#### (D) Smelt Additives

We believe that one of the most promising remedial measures to physical smelt-water explosions in chemical recovery furnaces is the maintenance of a small proportion of suitable material in smelt to render it non-explosive on accidental contact with water. As mentioned in previous reports, soda smelt (sodium-chloride free) consisting essentially of sodium carbonate, has never resulted in an explosion on contact with water under any plant or laboratory conditions.

Based on the physical encapsulation mechanism, it seemed reasonable to search for an "alloying" agent for the ceramic (kraft smelt) which would weaken solid smelt structurally and hence any encapsulating shell of frozen smelt which could form around a volume of water. In this manner the capsule walls would lack sufficient tensile strength to permit build-up of dangerous explosion pressures when water was introduced.

The true origin of the strength<sup>(2)</sup> of a metal or ceramic involves the forces or bonds between atoms. However, because of defects or imperfections which lead to high local stress concentrations when force is applied, the theoretical strength is never measured in an actual test. There have been numerous indications that impurities have a marked effect upon the mechanical properties of ionic crystals. However very few systematic studies of "alloying" additions to ceramics have been made. Recent investigations by others have shown that ceramic "alloys" behave in the same way as their metallic counterparts. Additions of small (as low as 0.1%) of foreign materials can either strengthen or weaken polycrystalline ceramics.

It was with this thought in mind that we began a systematic trial of additions to synthetic kraft smelt containing 30%  $\text{Na}_2\text{S}$ . A large variety of compounds of various elements in the periodic table have been tried. Effort has been made to vary widely the cation & anion size and charge to modify solid state strength. Dr. A.R.C. Westwood, Associate Director of the Research Institute for Advanced Studies (Baltimore, Md.) who is employed as a consultant on the project, suggested adding other alkali metal carbonates which have multiphase transformations on cooling. These may introduce discontinuities in the crystals and thereby form natural cleavage planes. Most additive candidates were chosen to meet the following qualifications: non-toxic, inexpensive, readily available, and non-interfering with the pulping and recovery cycle. The last qualification may prove the most difficult to meet. It will depend on the proportion required, whether the alloying agent is naturally eliminated in some part of the cycle, and the chemical changes involved in its transport through the various liquor streams. Here, an in-plant test for a successful laboratory-tested candidate may be required for final judgement about its effects on chemical recovery and pulp quality.

The general method of screening an additive was simply to melt 5% of it with the smelt, blend thoroughly and make a succession of 3 cc. injections of room temperature water from 1800° throughout the explosive range of smelt temperatures, approx. 1470-1670°F. The violence of the interaction(s) and the smelt temperature at which they occurred were recorded to compare effect of various additives.

Investigation of the change of physical properties is being made on cooled samples of the smelt for additives which radically affect the violent explosive behavior of molten smelt when water is injected into it.

A large number of smelt additives have been tested for explosion-preventing characteristics. These are listed in appended Table 2. It seemed feasible that a material which increased explosion tendency at one concentration in smelt might lessen it at another. Promising candidates were therefore tested over a range of concentrations. Generally the effective additives caused one of two changes in smelt-water interactions: either

they prevented explosions or they delayed the explosion to a lower (less violent) smelt temperature range. Usually, 15 or more 3cc room temperature water injections were necessary to solidify the smelt if no explosion resulted. Tests are grouped according to the major element involved.

Several conclusions may be drawn from this long list of compounds and results. Some compounds of the following elements appeared to have the tendency to lessen explosive violence: aluminum, calcium, cerium, chromium, cobalt, iron, magnesium, manganese, nickel, and strontium. Of these, aluminum and calcium seem particularly attractive because of effectiveness and price. The identities of both cation and anion of a compound were evidently important in determining effect of an additive. For instance, 5% calcium sulfide (#27) made explosions milder while 5% calcium fluoride (#28) produced one of the most violent explosions to date. Halides (chlorides, bromides, fluorides, etc.) invariably made smelt much more violent. Results from duplicate tests with a given additive were not entirely reproducible. It is believed that reproducibility will improve when the new automatic water injector is installed to replace the current manually-powered hypodermic syringe.

Changing cations also definitely modified the nature of the explosion. For instance 5% cadmium sulfide (#24) produced very violent explosions while 5% nickel sulfide (#74) gave only mild pops on 3 cc injections. There was evidence of an optimum range of concentrations for some materials. For instance in runs #73-76, nickel sulfide which retarded explosions at 2.5% and 5%, intensified them at 10%.

Perhaps the most promising lead is sodium aluminate ( $\text{NaAlO}_2$ ) tested in runs #11-18. This material noticeably increased smelt viscosity in concentrations as low as 1.25%. It was effective as low as 0.2% in retarding explosions if injections of water were made in slow succession, allowing each to evaporate before adding another.

Run #16 was made with water injections spaced so closely that one was added before its predecessor had evaporated from smelt surface. This produced a violent explosion at 1560°F. smelt temperature. Such behavior suggested that water on the smelt surface had dissolved smelt and the green liquor created had been forced beneath the smelt surface by a subsequent water injection. Runs #17 and #18 made using 10% green liquor with smelt containing 1 and 5%  $\text{NaAlO}_2$  (which had been adequate to prevent explosions with slowly spaced water injections) confirmed (a) the higher violence of green liquor injections and (b) the ineffectiveness of  $\text{NaAlO}_2$  to prevent explosions with this coolant. A successful smelt additive would have to prevent explosions with green liquor. Nevertheless,  $\text{NaAlO}_2$  is an interesting additive to study. Its modification of smelt properties is being examined in the hope that more complete knowledge of the inhibiting mechanism may facilitate finding a better inhibitor.  $\text{NaAlO}_2$  is readily soluble in smelt. A material soluble in aqueous alkaline solution might

be circulated unchanged through the pulping and recovery cycle, whereas those which form insoluble sulfides would be precipitated out in the green liquor dissolving tank. Much more makeup and/or processing would be required for this latter class of materials. Results from runs #55-64 implied that longer "cooking", i.e. maintenance in a molten condition, may have reduced  $\text{MnSO}_4$  to  $\text{MnS}$  by reaction with the graphite crucible. A five minute cook was the standard procedure.

### Strength of an Encapsulation Shell

Dr. A. R. C. Westwood thought it reasonable to expect greatly increased tensile strength of sodium carbonate due to various alloying agents employed and quoted as a parallel the 100-fold enhancement of the tensile strength of iron by suitable alloying additions. He mentioned also a rough figure of 25-fold additional improvement in the normally low tensile values of ceramics by reduction of surface imperfections (due to processes like the Joffe effect discussed in an earlier report) and also to the fine crystalline structure produced by very rapid chilling inherent in the encapsulation process.

A recent investigation of the effect of sodium chloride as an alloying agent on the compression strength of sodium carbonate has showed a direct parallel with the behavior of sodium sulfide in sodium carbonate reported earlier. Presence of 20% sodium chloride or 20% sodium sulfide in sodium carbonate makes the blend react explosively to injection of water. The compression strengths and hardness of  $\text{NaCl-Na}_2\text{CO}_3$  blends are given in Table 3 which follows:

TABLE 3

	<u>Composition</u> $\text{Na}_2\text{CO}_3$ -%-NaCl		<u>Compression Strength</u> (psi)	<u>Hardness</u> (Vickers Pyramid No.)
1)	100	0	997	9.9
2)	92.5	7.5	1860	17.9
3)	86.5	13.5	4800	20.1
4)	78.4	21.6	6060	18.0

Thus the strength of a sodium carbonate - sodium chloride blend (78.4 - 21.6) is more than six times that of sodium carbonate alone and its hardness is also greatly increased by such alloying.



## Future Work

The next item for laboratory work is a further sharpening of photographic technique based on suggestions from Mr. Frank C. Gibson, Mr. R. W. Watson, and Mr. J. E. Hay of the Bureau of Mines so that more detail is shown, especially of the capsule itself beneath smelt surface. Next, synthetic capsules of Pyrex glass and other materials will be made, immersed in smelt, and photographed, to see if parallel explosion behavior is exhibited. Ice pellets will also be tried for injection instead of water---as suggested by Dr. H. S. Gardner and the Bureau of Mines. The computer program for heat transfer into encapsulated water should be finished next month. This is expected to extend knowledge into a highly important area only postulated about before. Scaled-up explosion work in the spherical explosion test vessel will allow a more accurate separation of chemical from physical explosion energy than possible with currently used equipment.

Major emphasis will be placed on an exhaustive search for smelt additives effective against green liquor injection. Better knowledge of the reasons for even partially effective ones like sodium aluminate will no doubt facilitate the quest for practical anti-explosion additives for a chemical recovery furnace. Experiments will be made to produce very rapidly chilled smelt shells on which to determine physical properties. One way is to dip a hollow open-top water-filled aluminum or copper cylinder briefly into smelt to cast thin shells of smelt for strength and "metallographic" examinations. Further improvements in pressure wave measurement suggested by Mr. Frank C. Gibson of the Bureau of Mines will also be made.

## Expenditures on the C.E. Smelt-Water Explosion Study

Costs (cumulative) of the Combustion Engineering, Inc. study as of December 31, 1964 are itemized as follows:

Labor	\$20,350
Overhead	33,553
Materials	<u>24,574</u>
TOTAL	\$78,477

The amount billed to the sponsors as of December 31 was \$65,971.88. The actual rate of expenditure and that proposed are compared on the appended graph. The bills from purchase of several major items of equipment have caught up with billing so that the accumulated costs are running closer to estimated ones.

*Wharton Nelson*

WHARTON NELSON  
Senior Project Engineer  
February 12, 1965

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- (2) "Status of Ductile Ceramics Research" by  
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ASTM Publication No. 283, pp 52-65.

TABLE 2

SMELT ADDITIVES TRIED TO DATE

<u>ADDITIVE</u>		<u>%</u>	<u>EXPLOSION</u>	<u>SMELT TEMP. (°F) FOR EXPLOSION</u>
1 -	None	0	Violent	1650
2 -	"	0	Violent*	1585
3 -	AlPO <sub>4</sub>	5	Mild Pops	-
4 -	"	10	Sharp Expl.	1480
5 -	Al silicate (kaolin)	5	Violent*	1550
6 -	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	5	Pops	-
7 -	"	5	Moderate	1500
8 -	"	10	None	-
9 -	Al <sub>2</sub> O <sub>3</sub>	5	Violent	1600
10 -	"	5	Mild	1710
11 -	NaAlO <sub>2</sub>	5	Pops (viscous)	-
12 -	"	2.5	None (sl. viscous)	-
13 -	"	1.25	Mild Pops	-
14 -	"	0.5	None	-
15 -	"	0.2	Mild	1460
16 -	"	0.5	Violent (Injection in rapid succession)	1560
17 -	"	1	Violent (10% green liquor)	1600
18 -	"	5	Violent (10% green liquor)	1600
19 -	Sb <sub>2</sub> S <sub>3</sub>	5	Mild	1610
20 -	Ba(OH) <sub>2</sub>	5	Violent	1570
21 -	H <sub>3</sub> BO <sub>3</sub>	5	Violent	1640
22 -	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	5	Mild	1630
23 -	NaBr	5	<u>Very Violent</u>	1725
24 -	CdS	5	<u>Very*Violent</u>	1575
25 -	CaO	5	Mild	1430
26 -	CaSO <sub>4</sub>	5	Moderate	1520
27 -	CaS	5	Moderate	1535
28 -	CaF <sub>2</sub>	5	<u>Very Violent</u>	1650
29 -	CaCO <sub>3</sub>	5	Moderate	1470
30 -	"	7.5	Moderate	1470

\*Crucible was shattered

Table 2 (continued)

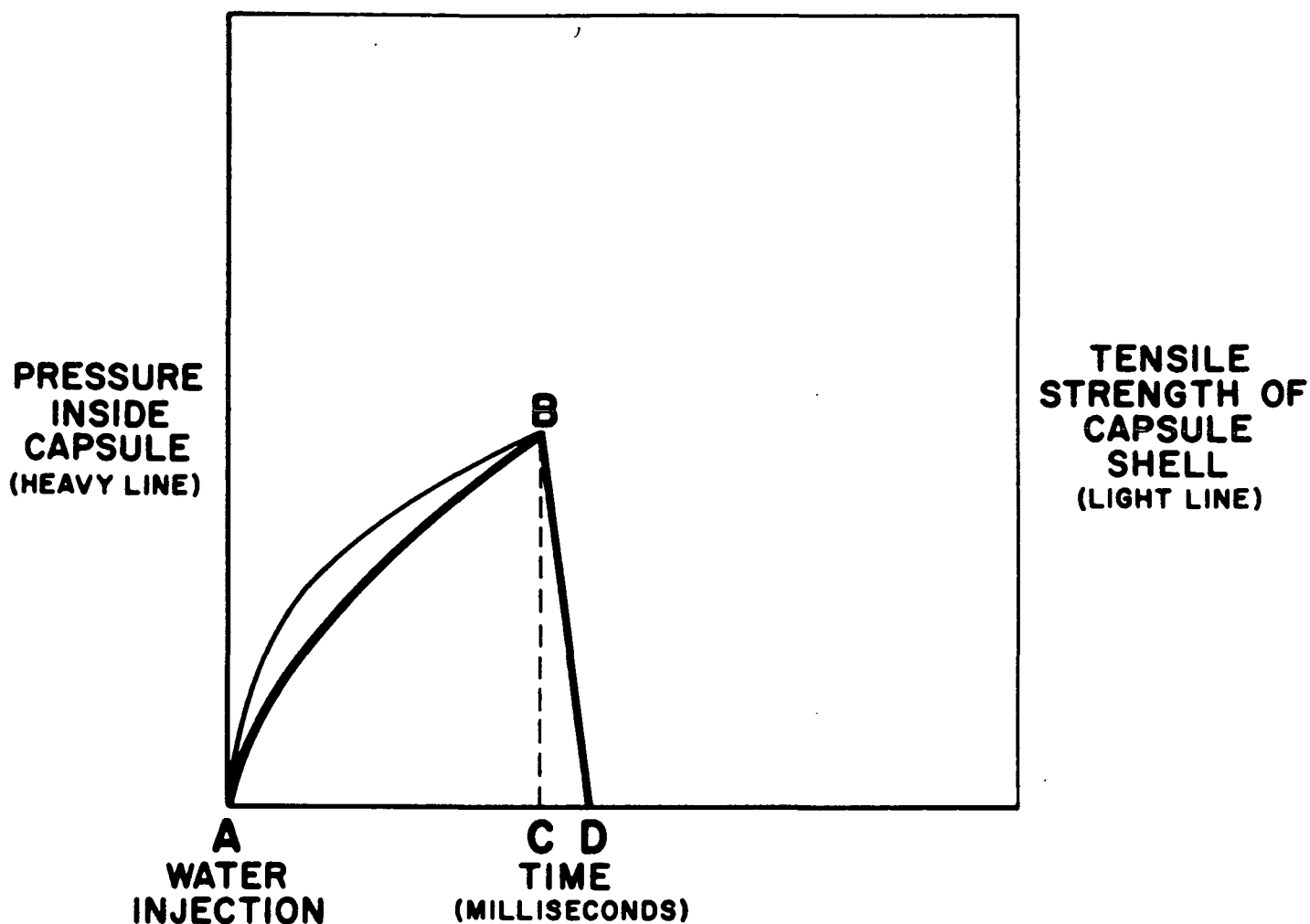
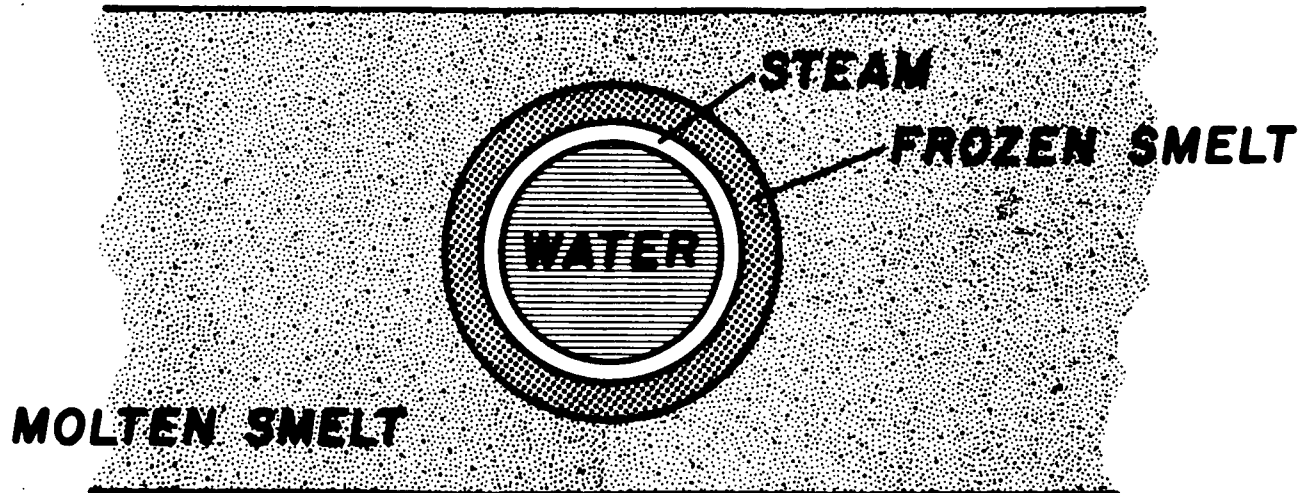
<u>ADDITIVE</u>		<u>%</u>	<u>EXPLOSION</u>	<u>SMELT TEMP. (°F) FOR EXPLOSION</u>
31 -	CaCO <sub>3</sub>	10	None	-
32 -	Carbon (fine)	5	Mild	1590
33 -	CeO <sub>2</sub>	5	Mild	1435
34 -	"	10	Mild	1550
35 -	Cr <sub>2</sub> O <sub>3</sub>	5	Violent	1615
36 -	Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	5	Moderate	1550
37 -	Na <sub>2</sub> CrO <sub>4</sub>	5	Mild	1510
38 -	Co <sub>2</sub> O <sub>3</sub>	5	Moderate	1510
39 -	CoS	3.9	Mild	1625
40 -	"	10	Muffled	1700
41 -	CoSO <sub>4</sub>	5	Violent	1500
42 -	CuO	5	Moderate	1625
43 -	FeS (fine)	5	Moderate	1695
44 -	Fe <sub>4</sub> (P <sub>2</sub> O <sub>7</sub> ) <sub>3</sub> (pyro)	5	Moderate	1430
45 -	Fe <sub>3</sub> O <sub>4</sub>	5	Moderate	1720
46 -	Green Liquor Dregs	5	Moderate	1620
47 -	Pb <sub>3</sub> O <sub>4</sub>	5	Violent	1460
48 -	Li <sub>2</sub> CO <sub>3</sub>	5	Violent	1730
49 -	Li <sub>2</sub> SO <sub>4</sub>	5	Mild spits	-
50 -	MgSO <sub>4</sub>	5	Mild	1550
51 -	MgO	5	Violent	1450
52 -	Mg silicate (Talc)	5	None	-
53 -	"	5	Mild	1560
54 -	MgCO <sub>3</sub> (fine)	5	Violent*	1580
55 -	MnSO <sub>4</sub>	2.5	Violent	1615
56 -	"	5	Moderate	1485
57 -	"	5	Pops	-
58 -	"	5	Violent	1685
59 -	"	5 (25 min. cook)	Mild	1585
60 -	"	20 (25 min. cook)	<u>Very*Violent</u>	1600
61 -	"	10	Mild	1425
62 -	MnS	2.5	Violent	1610

Table 2 (continued)

<u>ADDITIVE</u>		<u>%</u>	<u>EXPLOSION</u>	<u>SMELT TEMP.</u> <u>(°F) FOR EXPLOSION</u>
63 -	MnS	5	Mild	1630
64 -	"	10	Violent*	1640
65 -	Mn Acetate	5	Moderate	1470
66 -	" "	5	None	-
67 -	MnCl <sub>2</sub>	5	Violent	1660
68 -	MnCO <sub>3</sub>	5	Moderate	1490
69 -	"	10	Violent	1460
70 -	MoO <sub>3</sub>	5	Violent	1560
71 -	Ni Acetate	5	Violent	1675
72 -	NiSO <sub>4</sub>	5	Moderate	1485
73 -	NiS	2.5	Mild	1590
74 -	"	5	Pops	-
75 -	"	5	Pops	-
76 -	"	10	<u>Very Violent</u>	1675
77 -	Ni Titanate	5	Mild	1500
78 -	NiO	5	Moderate	1525
79 -	Na <sub>3</sub> PO <sub>4</sub>	5	Violent	1500
80 -	K <sub>2</sub> CO <sub>3</sub>	5	Violent	1730
81 -	"	26	Expl. with ea. G.L. inj.	-
82 -	"	69		-
83 -	K <sub>2</sub> SO <sub>4</sub>	5	Violent	1595
84 -	Na <sub>2</sub> SiO <sub>3</sub>	5	Violent	1580
85 -	SiC	5	Violent	1740
86 -	SiO <sub>2</sub> (fine)	5	Moderate	1710
87 -	SrO	5	Mild	1580
88 -	Na <sub>2</sub> SO <sub>4</sub>	10	Moderate	1450
89 -	"	13	<u>Very Violent</u>	1585
90 -	Na <sub>2</sub> S	8-40	Violence incr. % Na <sub>2</sub> S	
91 -	SnO <sub>2</sub>	5	Violent	1580
92 -	Na <sub>2</sub> SnO <sub>3</sub>	5	Moderate	1620
93 -	TiO <sub>2</sub>	5	Violent	1630
94 -	Na <sub>2</sub> WO <sub>4</sub>	5	Violent*	1600

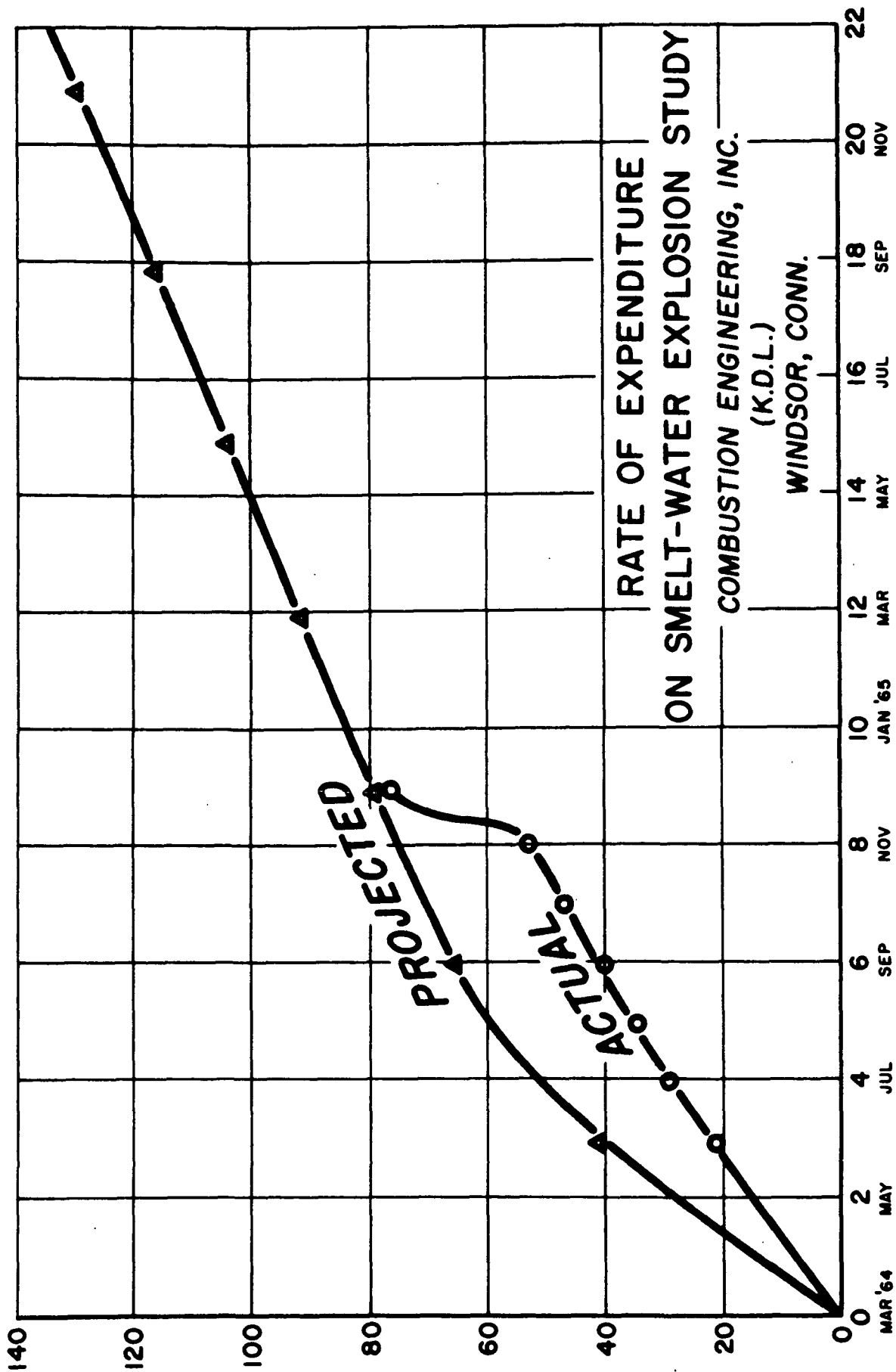
Table 2 (continued)

<u>ADDITIVE</u>		<u>%</u>	<u>EXPLOSION</u>	<u>SMELT TEMP. (°F) FOR EXPLOSION</u>
95 -	$\text{Na}_3\text{VO}_4$	5	Violent	1610
96 -	$\text{ZnO}$	5	Violent	1570
97 -	$\text{Zn}_3(\text{PO}_4)_2$	5	Mild	1525
98 -	$\text{ZrO}_2$	5	Violent	1700



**A THEORETICAL MODEL OF WATER  
ENCAPSULATION EXPLOSIONS IN MOLTEN  
KRAFT SMELT**

CUMULATIVE EXPENDITURE - THOUSANDS OF DOLLARS



RATE OF EXPENDITURE  
ON SMELT-WATER EXPLOSION STUDY

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MONTHS DURATION OF STUDY